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Measurement and Prediction of Binary Gaseous Diffusion Coefficients.

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Measurement and Prediction of Binary Gaseous Diffusion Coefficients

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The work was divided into three phases. The first phase consisted of designing all the necessary equipments for the investigation and set the process of securing them in motion. While they were being prepared or procured otherwise, an analysis of the existing experimental data was continued. The second phase started when the necessary hardwares were completed, and consisted of standardizing the equipments and calibrating the diffusion cell.

An account of the analysis of the existing experimental data and standardization of the equipments gathered for diffusion measurements was presented in the International Congress of Industrial Chemistry held in Brussels, Belgium in September, 1966 by Dr. Jesse Coates.

Another account of further analysis of the existing experimental data e.g. on the estimation of potential parameters was presented in the

Symposium of the American Institute of Chemical Engineers held in Houston, Texas, in February, 1967, again by Dr. Jesse Coates.

The third phase of the work consisted of measurement of effective diffusivities of certain systems carefully selected for the purpose, and of their conversion to true molecular diffusivities using the proper calibration factors of the diffusion cell. Examination of the measured data in the light of new analysis discovered in this work completed all phases of the present investigation.

Nevertheless, the problem of gas diffusion is not completely solved and a line of further action is suggested in the epilog.

The author wishes to appropriate this opportunity to express his heartfelt gratitude and indebtedness to Dr. Jesse Coates, Head Professor, and Dr. J. B. Cordiner, Associate Professor of Chemical Engineering of the Louisiana State University, for their invaluable guidance in the initiation and conduction of this investigation. He is further indebted to Dr. Jesse Coates for his kind permission to use the Transport Phenomena Research Laboratory and the departmental work-shop, and also for the necessary grants of fund supporting this investigation. His indebtedness extends to Dr. J. B. Cordiner for his untiring efforts to procure the materials and equipments needed for this work.

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Author

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ABSTRACT

An analysis of the existing experimental diffusion data led to the development of empirical prediction equations for binary gaseous systems, and empirical combining rules for the pure component potential parameters obtained from viscosity data. The correlations for the case of nonpolar-polar systems were not as good as for the case of nonpolar-nonpolar systems. This was thought to be due to the uncertainty existing in the values of individual parameters and consequently a direct method for their estimation was worked out. Some anomalies in the values of the parameters were discovered but the scattering of points in the correlations could not be removed. This suggested that the scattering of points in the correlations was possibly due to some property which is inherent in the polar molecules but has not been considered so far in the formulation of a potential function. It may be that the polar molecules have in addition to electric dipole moment a magnetic property that causes in addition to other already recognized forces, a magnetic force of attraction during unlike-molecular interactions.

A flow through porous plug method, such as the one reported by Scott and Cox, and Scott and Mian, was found, on thorough investigation, to be suitable for diffusion measurements of gaseous systems over a reasonable range of temperature. This technique, though not a direct one, gave effective diffusivities which were reproducible and had very small standard deviation and which when converted to true diffusivities agree with the ones measured by Walker and Westenburg and also with Hirschfelder's prediction equation. Diffusivities of N_2-HCl, A - HBr, and N_2 - HBr systems were measured under constant pressure condition as a function of

temperature and compared with those predicted by empirical equations as well as by Hirschfelder's equation.

INTRODUCTION

Binary diffusion coefficient has been defined by various authors in various ways. An excellent account of it is presented by Longwell and Sage[8]. The one adopted by Chapman and Cowling[2] appears to be more realistic than the others both from the point of view of its close agreement with the experiment for at least the idealized cases of non-polar nearly spherical molecules, as well as of its providing a clear picture of the mechanism of diffusion and assigning a physical significance to each of the causes of diffusion.

According to these authors, the general equation of diffusion for a binary system can be written in the following form:

$$\vec{C}_1 - \vec{C}_2 = -\frac{n^2}{n_1 n_2} D_{12} \left\{ \frac{\partial n_{10}}{\partial \vec{r}} + \frac{n_1 n_2 (m_2 - m_1)}{n\rho} \frac{\partial \log P}{\partial \vec{r}} - \frac{\rho_1 \rho_2 (\vec{F}_1 - \vec{F}_2)}{P\rho} + \frac{k_T}{T} \frac{\partial T}{\partial \vec{r}} \right\} \quad \text{Eq. 1.}$$

where $\vec{C}_1 - \vec{C}_2$ is the relative velocity of the molecule 1 with respect to molecule 2.

n, n_1, n_2 are number densities of the respective molecules, number of molecules per unit volume.

ρ, ρ_1, ρ_2 are the mass densities of the mixture, and pure components respectively,

$n_{10} = n_1/n$

m_1, m_2 are the molecular weights of components 1 & 2 respectively,

P is the pressure of the gas in consistent units,

$\vec{F}$, $\vec{F}_1$, $\vec{F}_2$ are the external forces on the molecules

k_T is the thermal diffusion ratio, D_T/D_{12}

D_T is the thermal diffusion coefficient in consistent unit,

T is the temperature of the gas in consistent unit,

D_{12} is the molecular diffusion coefficient.

This equation clearly indicates that diffusion may be caused by any one of the following factors e.g.

(1) non-uniformity of composition,

(2) non-uniformity of pressure,

(3) non-uniformity of temperature, and

(4) accelerative effects of the external forces on the molecules.

In absence of any external field force, non-uniformity of temperature and non-uniformity of pressure, the diffusion, caused only by non-uniformity of composition, can be measured experimentally with not much difficulty. However, diffusion due to non-uniformity of composition is effected by two driving forces rather than one e.g.

(1) concentration gradient, and

(2) inter molecular interactions.

These are inseparable from one another so that the effect of one cannot be exclusively observed by eliminating the other. Approximations, therefore, need to be introduced in order to observe the effect of intermolecular interactions.

It has been shown by various authors,[2],[3], in the cases of gases, that (1) the first approximation to the coefficient of diffusion does not depend on the concentration gradient, and

that (2) it depends only on encounters between molecules of different

kinds.

Encounters between molecules of the same kind have no effect upon diffusion.

Under these conditions the diffusion coefficient defined by Chapman and Cowling becomes identical to the one defined by Hirschfelder, Bird and Curtis[4]. Consequently, the prediction equation for the first approximation to the coefficient of diffusion due to later authors becomes in practical units:

$$\left[D_{12}\right]_1 = 0.0026280 \frac{\sqrt{T^3 (M_1 + M_2) / 2 M_1 M_2}}{P \sigma_{1,2}^2 \Omega^{(1,1)*}_{(T^*_{1,2})}} \qquad \text{Eq.2}$$

where $\left[D_{12}\right]_1$ is the first approximation to the coefficient of diffusion, cm^2 / sec.

P is pressure, atm.

T is temperature, °K

T^*_{12} is equal to $kT/\epsilon_{1,2}$, dimensionless

k is Boltzman constant, 1.3803×10^{-16} erg/(molecule) (°K)

M_1, M_2 are molecular weights of species 1 & 2 respectively

$\sigma_{1,2}$, $\epsilon_{1,2}$ are molecular potential energy parameters, characteristic of 1 - 2 interactions, Å and erg/(molecule).

$\Omega^{(1,1)*}_{(T^*_{12})}$ is collision integral, dimensionless.

If higher approximations to the coefficient of diffusion are desired, they can be obtained from the first approximation by multiplication with a certain correction function, $f^{(k)}_{D_{12}}$, as follows:

$$\left[D_{12}\right]_k = \left[D_{12}\right]_1 \int_{D_{12}}^{(k)} \qquad \text{Eq. 3}$$

The second approximation, therefore, is given by

$$\left[D_{12}\right]_2 = \left[D_{12}\right]_1 \int_{D_{12}}^{(2)}$$

The correction term, $\int_{D_{12}}^{(2)}$, is a function of

(a) the molecular weights of the two chemical species, M_1 and M_2,

(b) the concentration or mole-fraction of one relative to the other,

(c) the viscosities of the two components and of the mixture, and

(d) the temperature.

An explicit expression for this function shows that $\int_{D_{12}}^{(2)}$ is only slightly less than unity[4]. Hence the dependence of the coefficient of diffusion on the composition of a mixture of gases is only slight, so much so that with the accuracy of the experiments presently available for the measurement of gas diffusion, it is undetectable at least where the concentration is low.

For all practical purposes, therefore, Eq. 2 is the correct equation for the prediction of diffusion coefficients of binary gaseous systems. However, this equation presents a problem of having a previous knowledge of the pertinent unlike molecular interactions and of the correct potential energy function describing that interaction, in order that it can be used for prediction of coefficient of diffusion. This knowledge is not available at the present time. Although there exists a number of potential energy functions in the literature, their universal applicabilities

are debatable. For example, Lennard-Jones potential function,

$$\phi_{(r)} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad \text{Eq. 4.}$$

where $\phi_{(r)}$ is the potential energy of the molecule undergoing encounter,

σ is the distance parameter of the potential function or the distance between the centers of mass of the two molecules of the same kind undergoing encounter or collision, $\mathring{A}$,

ϵ is the energy parameter of the potential function or the depth of the potential well or the energy of the molecule at the time of collision, erg/(molecule)

This potential function is itself an approximation valid for like-molecular interactions between idealized molecules like those of inert gases, and nonpolar nearly spherical molecules of other gases.

The approach adopted by Hirschfelder, Bird and Curtis [4] for deriving a potential function, like that of Lennard-Jones, in order to describe the unlike-molecular interaction between two idealized, nonpolar nearly spherical molecules, by combining the potential functions, characteristic to the pertinent chemical species, requires a combining law for the individual parameters. One such law, arbitrarily made by the authors, e.g.

$$\sigma_{1,2} = \frac{\sigma_1 + \sigma_2}{2}$$

$$\epsilon_{1,2} = \sqrt{\epsilon_1 \epsilon_2} \qquad \text{Eq. 5}$$

although better than nothing, is liable to question. On the other hand, the potential energy function derived in this way e.g.

$$\phi_{(r)} = 4\epsilon_{1,2}\left[\left(\frac{\sigma_{1,2}}{r}\right)^{12} - \left(\frac{\sigma_{1,2}}{r}\right)^{6}\right] \qquad \text{Eq. 6}$$

has so far been able to predict the diffusion coefficients of binary systems, whose molecules are nonpolar and nearly spherical, within a reasonable limit of experimental values[13]. This is a remarkable success.

This potential energy function, however, is inadequate to predict diffusivities of systems which involve molecules that are polar and not nearly spherical. To cover the domain of nearly spherical polar molecules, Stockmayer[4] proposed a potential function, valid for like-molecular interactions, that is given by:

$$\phi_{(r)} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \frac{\mu^2}{r^3}\,g \qquad \text{Eq. 7}$$

where μ is dipole moment of the molecule

g is angular dependence of dipole-dipole interactions.

For unlike-molecular interactions, however, two cases may arise e.g.

(1) interaction between a polar and a nonpolar molecule, and

(2) interaction between two polar molecules of different chemical species.

Case - 1 : Polar - Nonpolar Systems

In this case instead of the dipole-dipole interaction there exists an interaction between the dipole moment of the polar molecule and the induced dipole, which is dependent on the polarizability, of the nonpolar

molecule. This nonpolar-polar molecular interaction, is independent of the angular orientation of the permanent dipole of the polar molecule and varies as the inverse sixth power of the distance. Thus the potential energy function for polar - nonpolar interactions, following Hirschfelder, Bird, and Curtis's approach, takes the form:

$$\phi_{(r)} = 4\,\epsilon_{1,2}\left[\left(\frac{\sigma_{1,2}}{r}\right)^{12} - \left(\frac{\sigma_{1,2}}{r}\right)^{6}\right] - \frac{\alpha_n\,\mu_p}{r^6} \qquad \text{Eq. 8}$$

where α_n is the polarizability of the nonpolar molecule.

Eq. 8 has been mathematically transformed by the later authors into the following form:

$$\phi_{(r)} = 4\,\epsilon_{np}\left[\left(\frac{\sigma_{np}}{r}\right)^{12} - \left(\frac{\sigma_{np}}{r}\right)^{6}\right] \qquad \text{Eq. 9}$$

where $\epsilon_{np} = \sqrt{\epsilon_1\,\epsilon_2}\;\xi^2$

$$\sigma_{np} = \left(\frac{\sigma_1 + \sigma_2}{2}\right)\xi^{-\frac{1}{6}}$$

$$\xi = 1 + \frac{1}{4}\,\alpha_n^*\,\mu_p^{*2}\sqrt{\frac{\epsilon_2}{\epsilon_1}} \qquad \text{Eq. 10}$$

$$\alpha_n^* = \alpha_n / \sigma_1^3$$

$$\mu_p^* = \mu_p / \left(\sqrt{\epsilon_2\sigma_2^3}\right)$$

Subscript 2 refers to the polar and 1 refers to the nonpolar molecule.

Eq. 9 has the same mathematical form as the Lennard-Jones potential function and hence the same collision integrals can be used for the pre-

diction of diffusivities of nonpolar-polar systems. However, Eq. 10 is still an arbitrary combining rule which is required to obtain the parameters of Eq. 9.

The predictions by Eq. 9, nevertheless, have been tested against experimental measurements and observed, except for a few systems which involve water or alcohols as the polar component, that they do not agree with experiment within a reasonable limit. This is evident from an analysis of the available experimental data (*).

Obviously closer investigations are needed.

Case - 2: Polar - Polar Systems

For the case of Polar - Polar systems, the angle dependent dipole-dipole interaction has been approximated by Mason and Monchick[11] using what is called a δ - factor. The resulting potential energy function e.g. the (12-6-3) potential:

$$\phi_{(r)} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} - \delta \left(\frac{\sigma}{r} \right)^{3} \right] \qquad \text{Eq. 11}$$

is again valid for like polar molecular interactions.

In order to adapt this Eq. 11 for unlike polar molecular inter-

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(*) Note: The approach of the analysis is explained in a separate chapter under PREDICTION while the outcome of it is presented in the form of Tables and Graphs in the section of Results.

actions following the approach of Hirschfelder, Bird and Curtis, it is necessary to invent a combining law for each of the three parameters e.g. ϵ, σ, and δ.

Furthermore, the validity of the resulting potential function e.g.

$$\phi_{(r)} = 4\,\epsilon_{p_1p_2}\left[\left(\frac{\sigma_{p_1p_2}}{r}\right)^{12} - \left(\frac{\sigma_{p_1p_2}}{r}\right)^{6} - \delta_{p_1p_2}\left(\frac{\sigma_{p_1p_2}}{r}\right)^{3}\right] \quad \text{Eq. 12}$$

has to be tested against experimental data which is not available at the present time.

It will, therefore, be extremely risky to develop prediction equation any further until more information about the behavior of the polar molecules is available from reliably accurate experimental measurements.

On the other hand, diffusion coefficient is an indispensable concept that is applied in various engineering operations and processes.

The primary objective of the present investigation is, therefore, confined in devising an experiment for the measurement of binary gas diffusion coefficients that would be simple to operate and yet accurate enough to interpret in terms of intermolecular interactions.

This investigation also aims to obtain an empirical correlation with the presently available diffusion data that would enable to predict the diffusion coefficients of polar-nonpolar systems in particular at least for the purposes of engineering works until an accurate theoretical prediction equation has been worked out.

An outline of the plan of investigation is given in the next section.

II. METHOD OF APPROACH

Initially it was planned that a survey be made of the current literature concerning the measurement and prediction of the diffusivities of binary gaseous systems in general and polar systems in particular. Also it was planned that an analysis of the data that are available in the literature at the present time be made in order to discover any trend or pattern, and that an attempt be made to obtain an empirical correlation that might serve as a means of predicting diffusivities of similar systems until such time that is necessary for the development of a suitable theoretical equation. This is given in the Section III under "Prediction of Diffusivities".

After a careful study of the available methods of measruement of diffusivities of binary gaseous systems, it was further planned that a suitable method be invented or selected and the apparatus be designed and fabricated. From a careful consideration it was decided that a flow method be employed and that a fritted glass porous solid be used as diffusion medium. This technique appeared to be simple and adaptable to any gas pair. The details are given in the Section IV, "Measurement of Diffusivities."

It was, in addition, planned that a set of gaseous systems be so selected that they involve only nonpolar nearly spherical molecules and that their diffusivities at various temperatures under constant pressure conditions are fairly accurately known, while a different set of systems be selected such that they involve nonpolar nearly spherical molecules as one component and polar nearly spherical molecules as another and that

their diffusivities at various temperatures are unknown. Consequently helium - argon, helium - nitrogen, and nitrogen - carbon dioxide were selected for the first set of systems while nitrogen - hydrogen chloride, argon - hydrogen bromide, and nitrogen - hydrogen bromide were selected for the second set of systems. The first set of systems, involving monatomic - monatomic, monatomic - diatomic, and diatomic - triatomic molecules, represented nearly spherical nonpolar molecules and their diffusivities had been measured by Walker and Westenburg[20] under extreme carefulness using the so-called point source technique. The second set of systems, involving monatomic - diatomic and diatomic - diatomic molecules, represented nearly spherical polar and nonpolar molecules and their diffusivities were unknown.

A lay-out of the flow sheet and a description and diagram of the diffusion apparatus are given in the section named MEASUREMENT OF DIFFUSIVITIES. Results of measurements for both the sets of systems are presented in Section - V, "RESULTS" and discussed in Section - VI, "DISCUSSIONS".

Sections - VII & VIII contain "BIBLIOGRAPHIC REVIEW" and "BIBLIOGRAPHY" respectively.

III. PREDICTION OF DIFFUSIVITIES

The theory for the prediction of transport properties of pure gases and gas mixtures has been sufficiently advanced in recent years. It has been observed that the Lennard-Jones (12-6) potential function is a fairly good representation of like-molecular interactions as long as the molecules in question are nonpolar and nearly spherical. It has further been established by now that for such molecules undergoing unlike molecular interactions the resultant potential function can also be represented by the same (12-6) type of potential as the Lennard-Jones and that the parameters of the resultant potential function can be obtained from the pure component data by using the combining rules adopted by Hirschfelder, Bird, and Curtis[4]; as given in Eq. 5.

The accuracy of prediction of diffusion coefficients for binary gaseous sytems involving nonpolar nearly spherical molecules using Hirschfelder's prediction equation, as reported by Sherwood and Reid[13], is within a reasonable limit of the experimental measurement (about 6%). However, the conventional approach toward the comparison of the predicted data to experimental ones is to calculate the Lennard-Jones (12-6) potential parameters for the pure components from viscosity or second virial coefficient data, obtain the same for the resultant potential by using the Hirschfelder's combining rule (Eq. 5.), and compare these parameters of the resultant potential with those calculated from diffusion data using similar techniques.

The calculation of these potential parameters from either viscosity, second virial coefficient, or diffusion data involves a trial and error

procedure and introduces a certain amount of uncertainty or error in the numerical values of those parameters. Graphical technique for the evaluation of potential parameters for like molecular interactions from viscosity data as proposed by Mason and Monchick[11] and that for unlike molecular interactions from diffusion data as adopted by Mian[10] and Scott, simplify the procedure to a great extent but does not eliminate the uncertainty in the values of the parameters.

The present work therefore aimed at deriving an empirical prediction equation that would give diffusion coefficients of binary systems with a minimum of uncertainty and an empirical combining rule for the potential parameters obtained from viscosity data in order to predict those of the resultant potential that would represent the unlike molecular interactions.

(a) ANALYSIS OF EXPERIMENTAL DATA AND DEVELOPMENT OF EMPIRICAL PREDICTION EQUATION:

The prediction equation for diffusion coefficient of binary gaseous systems, derived on the basis of kinetic theory of gases and expressed by Hirschfelder, Bird and Curtis[4] in practical units, as given by Eq. 2., on rearranging gives

$$\left[\sigma_{12}^2 \; \Omega^{(1,1)*}_{(T_{12}^*)} \right]_{\text{Diff.}} = \left[0.0026280 \; \frac{T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{P \, D_{12}} \right]$$

Eq. 13.

Whereas the right hand side of the above equation e.g.

$$\left[0.0026280 \; \frac{T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{P \, D_{12}} \right]$$

is calculable directly from a knowledge of M_1, M_2, T, P, and the measured diffusivity, D_{12}, the left hand side of the expression,

$$\left[\sigma_{12}^2 \quad \Omega^{(1,1)*}_{(T_{12}^*)} \right]$$

is predictable from a knowledge of the pertinent potential function. If the proper potential function is found, the group,

$$\left[\sigma_{12}^2 \quad \Omega^{(1,1)*}_{(T_{12}^*)} \right]_{\text{Pred.}}$$

is predicted for the particular temperature, T, and a plot of

$$\left[0.0026280 \; T^{3/2} \; \frac{\left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{P \; D_{12}} \right]_{\text{Expt.}}$$

versus

$$\left[\sigma_{12}^2 \quad \Omega^{(1,1)*}_{(T_{12}^*)} \right]_{\text{Pred.}}$$

be made, then a straight line with slope equal to unity would result. However, since the prediction of

$$\left[\sigma_{12}^2 \quad \Omega^{(1,1)*}_{(T_{12}^*)} \right]_{\text{Pred.}}$$

involves two assumptions, e.g.

(1) the assumed potential function, and

(2) the assumed combining rules for the potential parameters,

if the above plot gives a line with slope other than unity, any one or both of the assumptions made in the prediction may be wrong.

This plot therefore may serve as a simple test to determine if the experimental diffusion data fit the assumed potential function. It may be applied to individual systems as well as to all systems collectively thus giving a generalized correlation.

The experimental diffusion data of all nonpolar-nonpolar systems presently available in the literature were tested in a generalized plot by this technique for the Lennard-Jones (12-6) potential model. This is presented in the Section V, "RESULTS".

The test was also applied to the diffusion data of Nonpolar-Polar systems for both Lennard-Jones (12-6) potential as well as Stockmayer's (12-6-3) potential models. Results are presented in the partinent section.

This test, however, could not be applied to diffusion data of Polar - Polar systems as not enough data of such systems are available in the literature at the present time to justify such attempt for generalized correlations.

This test, however, is not of much utility other than the finding of right potential function. Also it involves the calculation of

$$\left[\sigma_{12}^2 \, \Omega^{(1,1)*}_{(T_{12}^*)} \right]_{\text{Pred.}}$$

for the assumed potential function. For simple potential functions like Lennard-Jones (12-6) or Stockmayer's (12-6-3), the collision integrals, $\Omega^{(1,1)*}_{(T_{12}^*)}$, are available as a function of T_{12}^* in the form of tables and graphs, where T_{12}^* is equal to kT/ϵ_{12}. But for complicated potential functions they are not available and are difficult to evaluate. It was therfore planned to develop a test

in terms of the parameters of potential function rather than collision integral.

Since in any case the collision integral, $\Omega^{(1,1)*}_{(T_{12}^*)}$, is an inverse function of T_{12}^* ,

$$\left[\sigma_{12}^2 \ \Omega^{(1,1)*}_{(T_{12}^*)}\right]_{\text{Pred.}}$$

should be a function of σ_{12}^2 / T_{12}^* and consequently,

$$\left[0.0026280 \ \frac{T^{3/2}\left(\frac{M_1 + M_2}{2M_1 M_2}\right)^{1/2}}{P \ D_{12}}\right]$$

should be a function of $\dfrac{\sigma_{12}^2}{T_{12}^*}$.

It was therfore decided to plot

$$\text{Log} \left[0.0026280 \ \frac{T^{3/2}\left(\frac{M_1 + M_2}{2M_1M_2}\right)^{1/2}}{P \ D_{12}}\right]$$

versus

$$\text{Log} \left[\frac{\epsilon_{12}\sigma_{12}^2}{kT}\right]$$

for the Lennard-Jones potential model for the cases of nonpolar-nonpolar systems and nonpolar-polar systems and the Stockmayer potential model for nonpolar-polar systems.

For the purpose of comparison

$$\left[\sigma_{12}^2 \ \Omega^{(1,1)*}_{(T_{12}^*)}\right]_{\text{Pred.}} \quad \text{versus} \quad \sigma_{12}^2 / T_{12}^*$$

are also shown in the same log-log plots as above.

The least square lines of these plots may then be used as empirical prediction equations for at least such time that is necessary for the development of truly theoretical equations.

The problem, however, remains in how to get the parameters of the resultant potential function that represents the unlike molecular interactions. This is discussed in the next two sub-sections.

(b) ESTIMATION OF POTENTIAL PARAMETERS:

Like Molecular Interactions:

The conventional approach for the estimation of parameters of any potential function for like-molecular interactions is to use viscosity or second virial coefficient data. The viscosity predicition equation as worked out by Hirschfelder, Bird and Curtis[4] is:

$$\eta \times 10^7 = 266.93 \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)*}_{(T^*)}} \qquad \text{Eq. 14}$$

where η = viscosity of a pure gas in gm./sec. cm.

M = molecular weight of the same gas,

T = temperature corresponding to the viscosity in °K,

σ = the distance parameter of the potential function in Å, and

$\Omega^{(2,2)*}$ = the pertinent collision integral.

(12-6) or Lennard-Jones potential function:

The general procedure to obtain the potential parameters is to assume ϵ/k, calculate $\frac{kT}{\epsilon}$ or T^*, obtain the corresponding $\Omega^{(2,2)*}$ from

the pertinent table or by performing the required integration, substitute in Eq. 14, and calculate σ^2 from known values of viscosity and temperature. If the same value of σ^2 is obtained at different temperatures, the assumed value of ϵ/k is correct. On the other hand if the values of σ^2 are not the same, a different value of ϵ/k is assumed and the trial is continued until the same value of σ and ϵ/k satisfy Eq. 14 at all temperatures.

This is a time consuming and tiresome process. A somewhat short-cut method proposed by Mason and Monchick[11] is one that involves graphical trial and error technique. In this method a plot of

$$\text{Log}\left(T^{*3/2}\,\Omega^{(2,2)*}_{(T^*)}\right) \quad \text{versus Log } T^*$$

and another plot of

$$\text{Log}\left(266.93 \times 10^{-7}\,\frac{\sqrt{MT}}{\eta}\right) \text{versus Log } T$$

are prepared on two sheets of transparent papers. The second plot is then superposed on the first and the values of T^* that correspond to each temperature T (or in other words the amount of translation of origin along the T or T* axis) are obtained which enables ϵ/k to be calculated. The evaluation of σ still involves the same technique as in analytical trial and error method.

The present method is somewhat analogous to Mason and Monchick's except for the fact that instead of graphical superposition, an analytical comparison of the slopes of the two curves is affected. This is in essence a combination of graphical and analytical technique and is effected in the following DIRECT METHOD.

(i) DIRECT METHOD:

The viscosity prediction equation, Eq. 14, on rearranging becomes

$$\left[\sigma^2\ \Omega^{(2,2)*}_{(T^*)}\right] \quad = \quad \left[266.93 \times 10^{-7}\ \frac{\sqrt{MT}}{\eta}\right] \qquad \text{Eq. 14a}$$

the left hand side of which is predictable from pertinent potential function while the right hand side is obtainable from experimental measurements.

$\Omega^{(2,2)*}_{(T^*)}$ is an inverse function of $\frac{kT}{\epsilon}$ or T^*. Assuming that in small ranges of T^*, $\log \Omega^{(2,2)*}_{(T^*)}$ is linear with $\log T^*$ i.e.

$$\log\ \Omega^{(2,2)*}_{(T^*)} = A_o - m \log T^*, \quad \text{for } T_1^* < T^* < T_2^*$$

Where A_o is intercept and m is the slope of the line, and

$$\left(T_2^* - T_1^*\right) \text{is small,}$$

the slope, m, for each small interval of T^*, can be computed as

$$-m = \frac{\Delta \log \Omega^{(2,2)*}}{\Delta \log T^*} = \frac{d \log \Omega^{(2,2)*}}{d \log T^*} \qquad \text{Eq. 15}$$

Assigning the value of $\underline{-m}$ to the average value of T^*_{avg}, defined by $T^*_{avg} = \frac{T_2^* + T_1^*}{2}$

a table of -m against T^*_{avg} or a plot of -m versus T^*_{avg} can be prepared for the potential function for which $\Omega^{(2,2)*}_{(T^*)}$ values are available. This table or plet can then be used as reference for subsequent use in the estimation of the potential parameters.

Now considering the right hand side of Eq. 14a, viz.

$$\left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right]$$

determined experimentally, should be equal to equal to

$$\left[\sigma^2 \, \Omega^{(2,2)^*}_{(T^*)} \right]$$

provided the right potential function is found.

Since σ is independent of T^*,

$$\left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right]$$

should be the same function of T^* as $\Omega^{(2,2)^*}_{(T^*)}$ is of T^*. Therefore, for small ranges of T^*, it may be assumed that

$$\text{Log} \left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right] = B_o - n \log T^* \qquad \text{Eq. 16}$$

Where B_o is the intercept and -n is the slope of the line.

But $T^* = \frac{kT}{\epsilon}$, and

$$\text{Log} \quad T^* = \text{Log } T - \log \frac{\epsilon}{k} \qquad \text{Eq. 17}$$

Therefore

$$\left[\log \left(266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta}\right) \right] = B_o - n \left(\text{Log } T - \log \frac{\epsilon}{k}\right)$$

$$= C_o - n \log T$$

On differentiating

$$\frac{d \log \left(266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right)}{d \log T} = -n \qquad \text{Eq. 18}$$

For the right potential function -m should be equal to - n. The slope, - n, obtained from experimental plot, is valid within

the temperature range $T_2 - T_1$. It can therefore be assigned to an average value of temperature defined by

$$T_{avg} = \frac{T_2 + T_1}{2} \qquad \text{Eq. 19}$$

At -m = -n, compatible values of T^*_{avg} and T_{avg} are obtained and the energy parameter of the potential function for the particular gas is calculated as

$$\frac{\epsilon}{k} = \frac{T_{avg}}{T^*_{avg}} \qquad \text{Eq. 20}$$

For the case of Lennard-Jones or (12-6) potential, since there is only one value of $\Omega^{(2,2)*}_{(T^*)}$ corresponding to each T^*, a unique value of the energy parameter ϵ/k can be obtained. After thus establishing the energy parameter, ϵ/k, σ^2 value can be calculated by dividing

$$\left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right] ,$$

computed at T_{avg}, by the $\Omega^{(2,2)*}_{(T^*)}$ corresponding to the T^*_{avg}.

(12-6-3) or Stockmayer Potential Function:

Where there is an encounter between two molecules, be they of the same kind or different but have permanent dipole moments in them, a (12-6-3) type or Stockmayer potential is usually necessary to express their behavior. When molecules of the same kind are involved i.e. in the like molecular interactions, the potential function $\phi_{(r)}$ assumes the form given by Eq. 7. This equation has an angle de-

pendent correction term, g, which makes it difficult to use in the prediction of transport properties of gases. Mason and Monchick[11] have converted it to a usuable form by using an angle independent correction term, δ_{max}. This is given by Eq. 11, and δ_{max} is defined by

$$4 \epsilon \sigma^3 \delta_{max} = 2 \mu^2 \qquad \text{Eq. 21}$$

where μ = dipole moment, debye, and

ϵ, σ = the energy and distance parameters of the potential function respectively.

Mason and Monchick[5] have evaluated the collision integrals $\Omega^{(2,2)*}_{(T^*)}$ and $\Omega^{(1,1)*}_{(T^*)}$ for various values of δ_{max} and T^* and presented them in the form of tables.

The use of (12-6-3) potential function, therefore, involves the estimation of three parameters e.g. ϵ, σ, and δ_{max}. The conventional trial and error approach becomes still more tedious and time consuming. However, this can be done easily in the following.

(ii). DIRECT METHOD:

Step - 1: A reference plot of $\frac{d \log \Omega^{(2,2)*}}{d \log T^*}$ or - m versus T^*_{avg} is prepared for each δ_{max}. This gives a family of curves.

Step - 2: A plot of log $\left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta}\right]$ versus log T is prepared from experimental data, and the slope, - n, is determined.

Step - 3: At - m = - n, corresponding to each δ_{max}, there

is obtained a T^*_{avg} value.

Step - 4: For each δ_{max}, using the corresponding T^*_{avg}, T_{avg}, dipole moment, μ, and Boltzman constant, k, σ^2 is evaluated using Eq. 21, or its equivalence in practical units viz.

$$\sigma^3 = 3622.0 \frac{\mu^2}{(\epsilon/k)(\delta_{max})} \qquad \text{Eq. 21a}$$

Step - 5: Corresponding to each δ_{max} and T^*_{avg}, $\Omega^{(2,2)*}_{(T^*)}$ is obtained from pertinent table and $\left\{ \sigma^2 \, \Omega^{(2,2)*}_{(T^*)} \right\}_{avg.}$, is computed and plotted against δ_{max}.

Step - 6: Corresponding to T_{avg}, $\left[266.93 \times 10^{-7} \frac{\sqrt{MT}}{\eta} \right]$, which is equivalent to experimental $\left\{ \sigma^2 \, \Omega^{(2,2)*}_{(T^*_{avg})} \right\}_{avg.}$ is calculated. δ_{max} is then obtained from the plot of step-5, corresponding to $\left\{ \sigma^2 \, \Omega^{(2,2)*}_{(T^*_{avg})} \right\}_{avg}$

Step - 7: Corresponding to the δ_{max} and - m = - n, T^*_{avg} is obtained from the reference plot of Step-1.

Step - 8: Corresponding to the obtained T^*_{avg} and δ_{max}, $\Omega^{(2,2)*}_{(T^*_{avg})}$ is obtained from pertinent table and σ^2 (or σ) is calculated as in the case of (12-6) potential.

Step - 9: ϵ/k value is then calculated from the relation

$$\frac{\epsilon}{k} = \frac{T_{avg}}{T^*_{avg}}$$

(c) ESTIMATION OF POTENTIAL PARAMETERS:

Unlike Molecular Interactions:

Unlike-molecular interactions may be grouped into three catagories e.g.

(1) encounters involving two kinds of molecules both of which follow 12-6 potential functions in their respective pure states, viz. nonpolar-nonpolar interactions;

(2) encounters involving two kinds of molecules one of which follows 12-6 potential while the other follows 12-6-3 potential functions in their respective pure states viz. nonpolar-polar interactions; and

(3) encounters involving two kinds of molecules both of which follow 12-6-3 potential functions in their respective pure states, viz. polar-polar interactions.

These interactions are involved in molecular diffusion. Consequently binary diffusion data would be a good source for the estimation of the potential parameters involved in unlike molecular interactions. However, diffusion data are difficult to obtain and usually are scanty. It is often desired to predict diffusivity from informations regarding the system obtained elsewhere. It would therefore be most convenient if the parameters of the potential function involved in the unlike-molecular interactions could be predicted from pure component parameters.

Hirschfelder, Bird and Curtis have developed a cominging rule for the parameters obtained from like - molecular interactions in order to predict those for unlike - molecular interactions, provided the interactions follow the 12-6 type of potential functions.

(12-6) type or Lennard Jones potential function:

Prediction rules: If σ_1 and ϵ_1 are the parameters of 12-6 type of potential function involving like-molecular interactions of the chemical species, 1, and if σ_2 and ϵ_2 are similar parameters for chemical species, 2, then the corresponding parameters of the 12-6 type of potential function involving unlike-molecular interactions between the chemical species 1 and 2, would be

$$\left.\begin{aligned} \sigma_{12} &= \frac{\sigma_1 + \sigma_2}{2} \\ \epsilon_{12} &= \sqrt{\epsilon_1 \epsilon_2} \end{aligned}\right\} \qquad \text{Eq. 5}$$

These rules are arbitrary but they have been found to give a fairly good estimate of the true parameters for the unlike-molecular interactions especially in the cases of nonpolar-nonpolar nearly spherical molecules. However, if it is desired to compare the predictions with the true values of these parameters i.e. if it is desired to check the universal validity of the Hirschfelder's combining laws it is necessary to estimate the true values of the parameters from diffusion data. This is done in the following way.

Estimation technique: Analogous to Mason and Monchick's graphical technique for the evaluation of the potential parameters involving like-molecular interactions from viscosity data, there is Mian[10] and Scott's graphical technique for the estimation of parameters involving unlike-molecular interactions from diffusion data. This involves in making a reference plot of $\log \Omega^{(1,1)^*}_{(T^*_{12})}$ versus $\log T^*_{12}$, in superposing onto it a plot of

$$\text{Log} \left\{ \frac{0.0026280\, T^{3/2}}{D_{12}\, P} \left(\frac{M_1 + M_2}{2M_1 M_2} \right)^{1/2} \right\} \text{ versus Log T,}$$

prepared from experimental diffusion data, and in matching T^*_{12} and T values.

The energy parameter $\frac{\epsilon_{12}}{k}$ is then obtained as

$$\frac{\epsilon_{12}}{k} = \frac{T}{T^*_{12}}$$

The remainder of the procedure is exactly the same as described under like-molecular interactions.

Direct Method: A method analogous to the presently described direct method for the extimation of the potential parameters involved in the like-molecular interactions, can now be developed for those involved in unlike-molecular interactions using Hirschfelder's equation for prediction of diffusion coefficients. Hirschfelder's equation on rearranging assumes the following form:

$$\left[\sigma^2_{12}\,\Omega^{(1,1)^*}_{(T^*_{12})}\right] = \frac{0.0026280\; T^{3/2}\left(\frac{M_1 + M_2}{2M_1 M_2}\right)^{1/2}}{D_{12}\, P} \qquad \text{Eq. 13}$$

which is comparable with Eq. 14a.

Therefore, following the same technique as with Eq. 14a, a reference table or plot can be made with the slope

$$-m \left(= \frac{d \log \Omega^{(1,1)^*}}{d \log T^*_{12}}\right) \text{ versus } T^*_{12} .$$

Then using the experimental data,

$$n = - \frac{d \log \left[\frac{0.0026280\ T^{3/2} \cdot \left(\frac{M_1 + M_2}{2M_1 M_2} \right)^{1/2}}{D_{12} P} \right]}{d \log T}$$

can be computed in the same way as with the viscosity data.

At $- m = - n$, $(T^*_{12})_{avg}$ corresponds to T_{avg} and consequently

$$\frac{\epsilon_{12}}{k} = \frac{T_{avg}}{(T^*_{12})_{avg}}$$

(12-6) or Lennard-Jones potential involving molecules one of which follow a 12-6-3 or Stockmayer's potential function in its pure state:

Prediction rules: If σ_1 and ϵ_1 are the parameters of 12-6 type of potential function involving like-molecular interactions of the chemical species, 1, and if σ_2 , ϵ_2 and $\delta_{max,2}$ are similar parameters of the 12-6-3 potential function for like-molecular interactions of the chemical species, 2 then the corresponding parameters of the 12-6 type of potential function involved in the unlike-molecular interactions between the chemical species 1 and 2 would be

$$\epsilon_{np} = \sqrt{\epsilon_1 \epsilon_2}\ \xi^2$$

$$\sigma_{np} = \left\{ \frac{\sigma_1 + \sigma_2}{2} \right\} \xi^{-1/6}$$

and $$\xi = \left[1 + \frac{1}{4}\ \alpha_n^*\ \mu_p^{*2}\ \sqrt{\frac{\epsilon_2}{\epsilon_1}} \right] \qquad \text{Eq. 10}$$

where $\alpha_n^* = \frac{\alpha_n}{\sigma^3}$, $\mu_p^* = \frac{\mu_p}{\sqrt{\epsilon_2 \sigma_2^3}}$; α_n = polarizability of molecules of 1 and μ_p = dipole moment of molecules of 2.

Unlike nonpolar - nonpolar systems, this arbitrary prediction rule does not give any good estimate of the true parameters for nonpolar-polar systems.

Estimation technique (Direct Method): The estimation of the parameters for the 12-6 type of potential from experimental diffusion data would involve the same technique as used in the case of nonpolar-nonpolar systems.

12-6-3 or Stockmayer's potential function involving molecules both of which follow 12-6-3 potential functions in their pure states:

No prediction rule (i.e. combining laws of the pure component parameters) for the parameters of 12-6-3 potential involving unlike molecule interactions have yet been worked out. Also not enough experimental diffusion data is available in the literature to test the validity of any prediction rules.

The estimation of the parameters, however, can be made from experimental diffusion data using the similar technique as used in the case of pure component parameters from viscosity data, i.e. by following the steps outlined under like-molecular interactions involving 12-6-3 type of potential function except the following:

(step - 2), Log $\left[0.0026280 \frac{T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{1/2}}{D_{12}P} \right]$ vs. Log T is used instead of

$$\text{Log}\left[\, 266.93 \times 10^{-7}\ \frac{\sqrt{MT}}{\eta}\ \right] \quad \text{vs Log T}$$

$$\text{(step - 4)}, \quad 4\,\epsilon_{12}\,\sigma_{12}^{3}\,\delta_{12,\max} = 2\mu_1\mu_2$$

$$\text{or} \quad \left[\frac{\delta_{12,\max.} \times 2k}{T_{12}^{*}}\right] = \frac{\mu_1\ \mu_2}{\sigma_{12}^{3}\ T_{avg.}} \qquad \text{Eq. 2}$$

is used instead of

$$\left[\frac{\delta_{max.} \times 2k}{T^{*}}\right] = \frac{\mu^2}{\sigma^3\ T_{avg.}}$$

$$\text{or} \quad \sigma_{12}^{3} = 3622.0\ \frac{\mu_1\ \mu_2}{(\epsilon_{12}/k)(\delta_{12,\ Max.})}$$

(d) CORRELATION OF THE POTENTIAL PARAMETERS OBTAINED FROM VISCOSITY DATA WITH THOSE OBTAINED FROM DIFFUSION DATA:

Once the pure component potential parameters are determined accurately from experimental viscosity data and combined parameters from experimental diffusion data, an empirical combining rule can be obtained from a generalized correlation of these two types of parameters. One such correlation would be a plot of Log ϵ_{12} versus log $\epsilon_1\epsilon_2$, and a plot of σ_{12} versus $(\sigma_1 + \sigma_2)$. ϵ_{12} is estimated from diffusion data while ϵ_1 and ϵ_2, from viscosity data. Similarly σ_{12} is obtained from diffusion while σ_1 and σ_2 from viscosity data.

IV. MEASUREMENT OF DIFFUSION COEFFICIENTS

Accurate measurements of binary gas diffusion coefficients of Polar-Nonpolar systems as a function of temperature under constant pressure conditions are felt necessary for two fold reasons, e.g.

(1) such data will throw some light in the understanding of the nature of polar - nonpolar molecular interactions which is important for the development of a suitable theory for the prediction of transport properties of gases, and

(2) it will help to develope an empirical prediction equation for the transport properties such as the ones described under the Section-III, "Prediction of Diffusivities", which is badly needed in engineering works for at least such time that is necessary to develope an adequate theory.

A number of different techniques are available in the literature for the measurement of gas diffusion coefficients but not all of them are suitable for all gases nor all for different temperature measurements. Some of them are easy to operate but not precise enough in results while the others have precision in results but difficult to operate. Examples of the 1st type is Loschmidt Cell[9] and that of the 2nd is the Walker and Westenburg's so called Point Source Technique[20].

The one selected for the present investigation e.g., Porous plug diffusion cell, is easy to operate and suitable for all nearly spherical molecules. This technique first proposed by Wicke and Kallenbach[22], modified by Weisz[21] for measuring effective diffusivities in catalytic particles, adapted by Scott and Cox[15], Scott and Dullien[16] and Scott

and Mian[10] for the measurement of binary gas diffusion coefficients was further modified and improved.

(a) APPARATUS

The apparatus required may be grouped into three catagories e.g.

(1) one in which diffusion operation is achieved, called the Diffusion Cell,

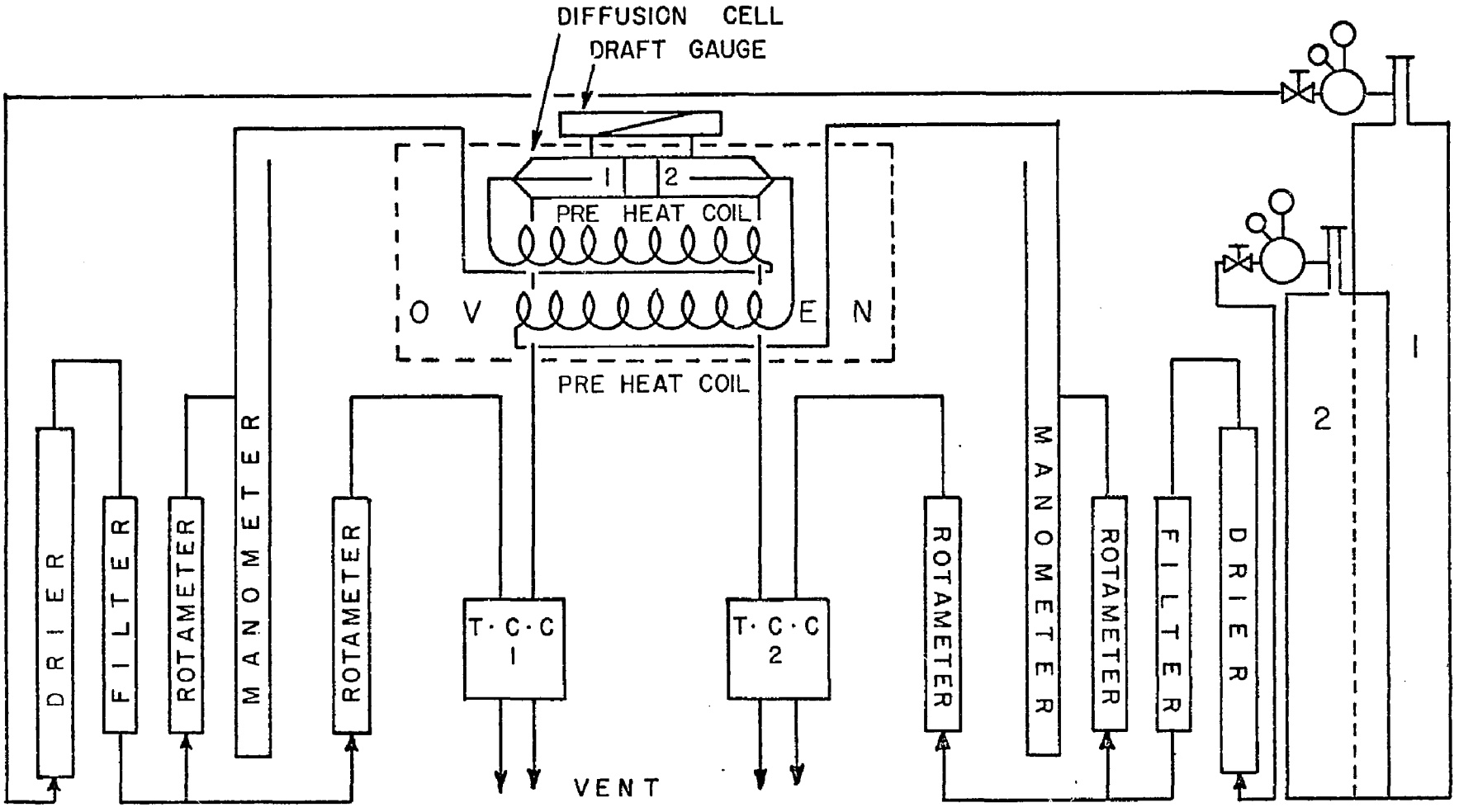
(2) one in which analysis is made of the gas streams after the diffusion has taken place, and

(3) other accessories.

A lay-out of the qualitative flow-sheet is given in Figure-1.

Group-1: Diffusion Cell

A sketch of the diffusion cell is given in figure-2. It is made up of a pyrex glass tube of 1.27 cm. diameter and 25.4 cm. length. A fritted glass porous plug of 1.27 cm. length and a nominal pore size of 10 micron, built in the middle of the glass tube, divides it into two compartments viz. 1 and 2. Each compartment is provided with an inlet for the entrance of a pure gas stream, and an outlet line for the exit of the stream after diffusion. Both compartments are connected to a draft gauge which serves to detect any inbalance of pressure between them. Each inlet line is connected to a pre-heating coil also made of pyrex glass tube of 8 mm. diameter and 244 cm. length. The whole assembly is mounted on a platform and housed inside an electrically heated, and electronically controlled, forced air circulation oven. The inlet and outlet lines to the diffusion cell pass through the holes in the oven door. The draft gauge is mounted on the oven door and the connecting lines between draft gauge



FLOW SHEET FOR DIFFUSION MEASUREMENT

FIGURE - 1

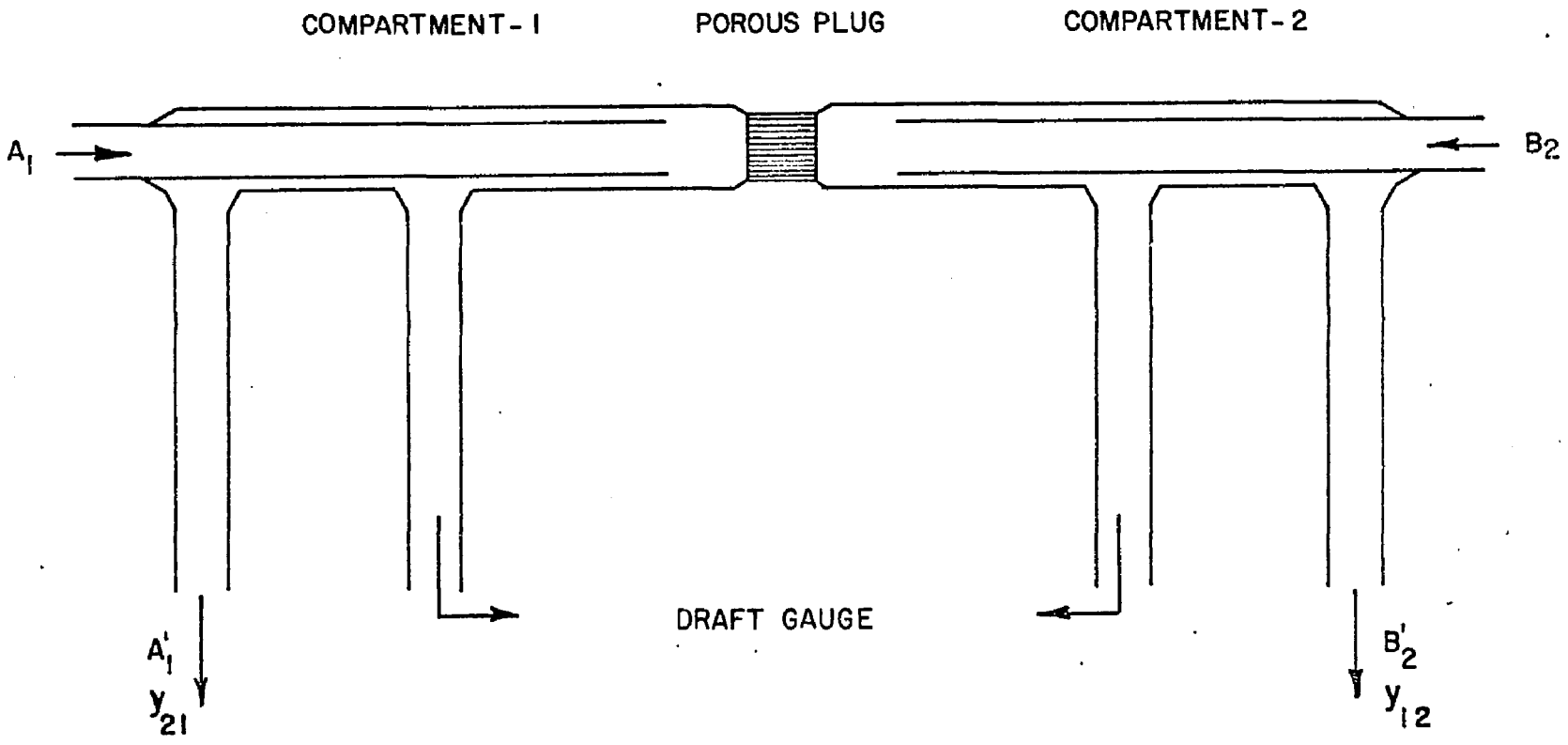


FIGURE - 2· DIFFUSION CELL

and diffusion cell are led through holes in the door.

The oven was designed and constructed in the Department of Chemical Engineering, Louisiana State University. The top and front views of the oven are shown in figures -3 & 3A.

Group-2: Analytical Equipments

For the analysis of the two streams leaving the diffusion cell two diffusion type thermal conductivity cells are used. A sketch of the Gow-Mac made T.C. Cell is given in Figure - 4.

Each T.C. Cell is provided with two inlet and two outlet lines for flow of reference and sample gases. Both the T.C. Cells are housed in a water bath of constant temperature, controlled within a degree centigrate by using a mercury regulator. Any effect, due to temperature variation of the surrounding of the T.C. Cells by 1°C, on the output of analysis is compensated for by mechanical design of the T.C. Cells. A pre-heating coil made of 8 mm. pyrex glass tube is attached to each inlet line of the T.C. Cell and housed in the same water bath.

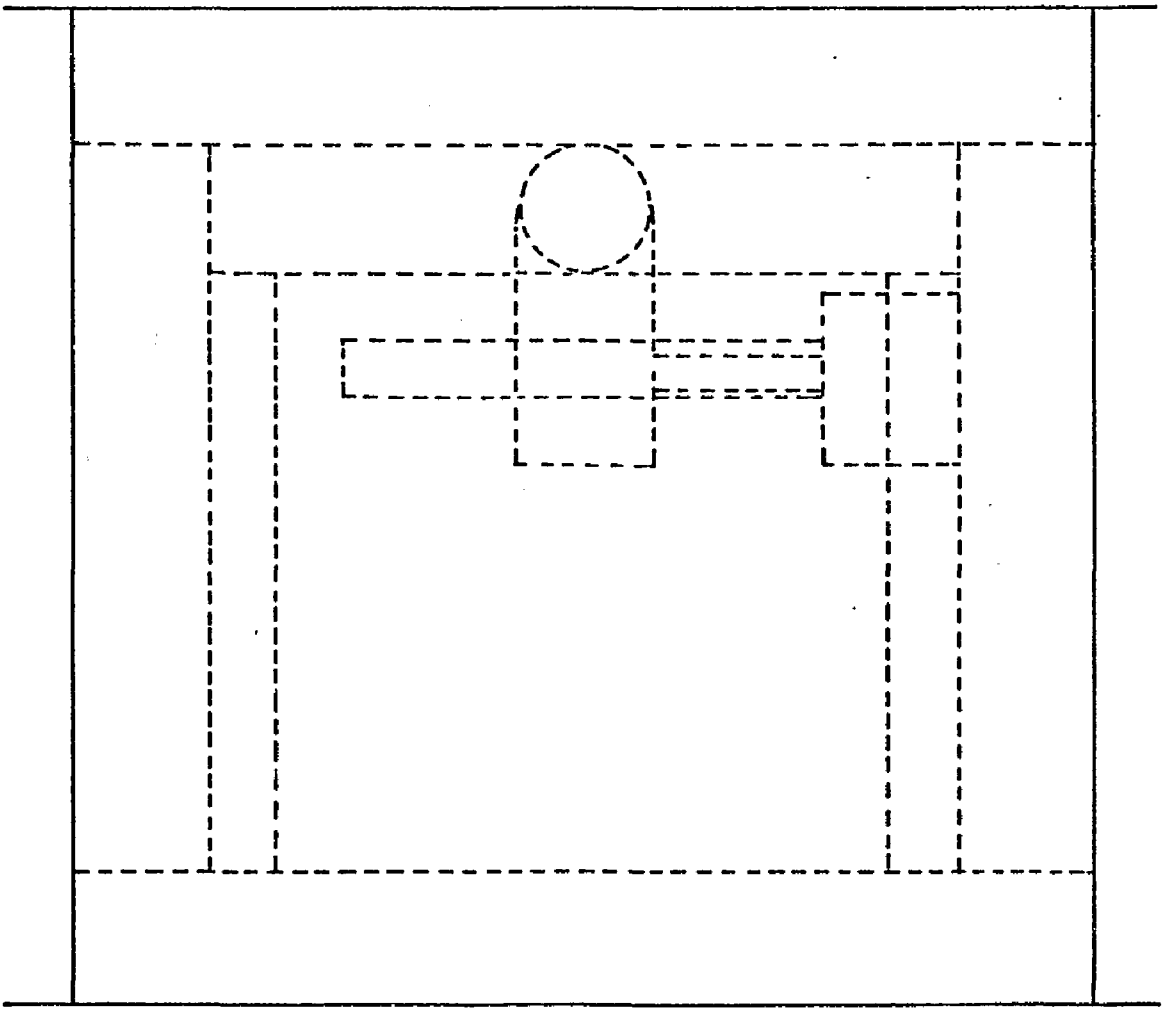
The T.C. Cells are supplied with electric power under electronically controlled D.C. voltage from Gow-Mac Power Supply Units which are also provided with mechanism of attinuation of the signal obtained from the T.C. Cells during the process of analysis. Electrical wiring diagram is shown in Figure - 5.

Group-3: Accessories

Amongst other accessories the following may be mentioned:

(a) a research grade Fortin's barometer,

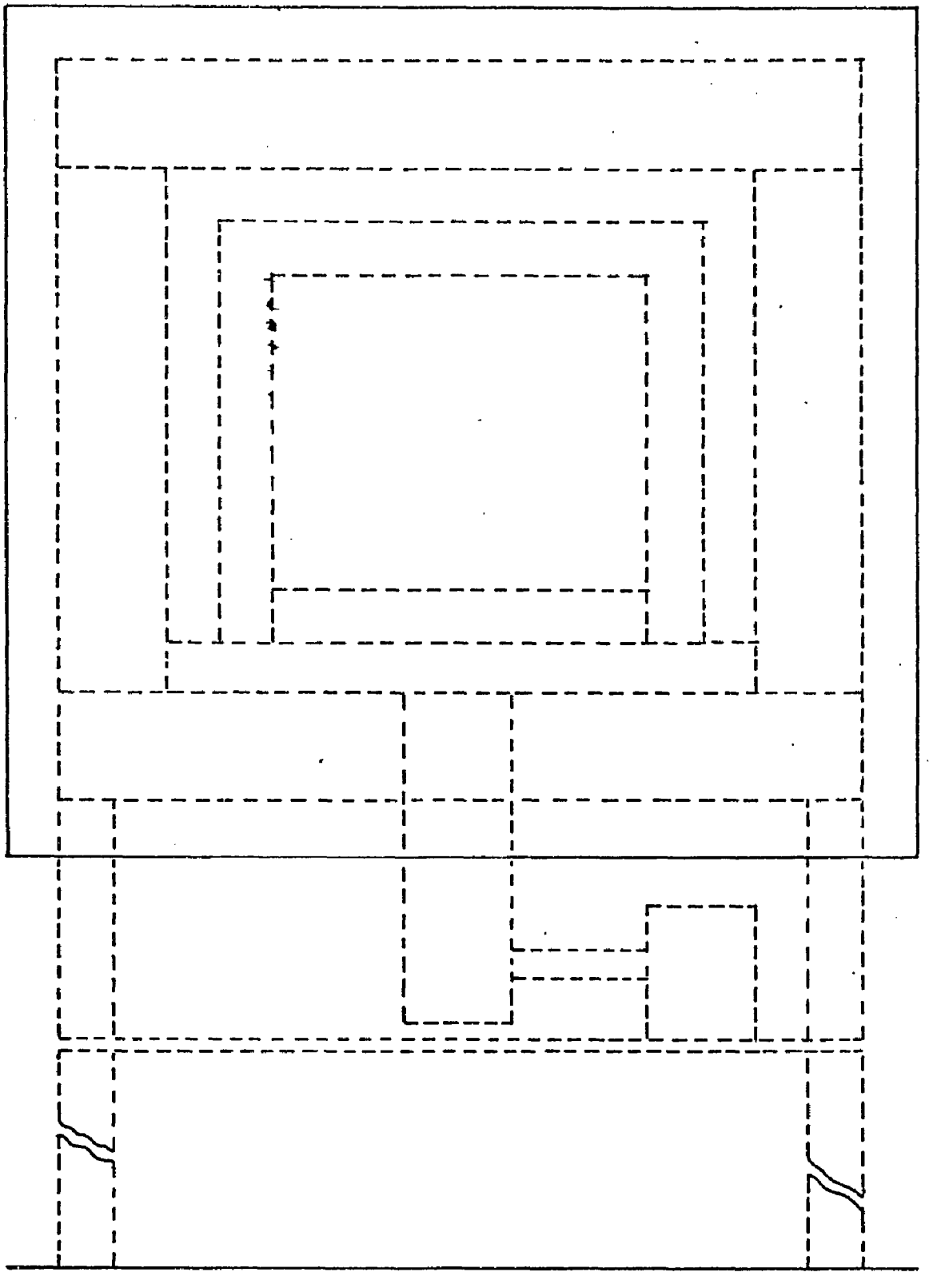
(b) a wet test meter



TOP VIEW OR

PLAN

FIGURE - 3. OVEN



FRONT VIEW OR
ELEVATION

FIGURE - 3A. OVEN

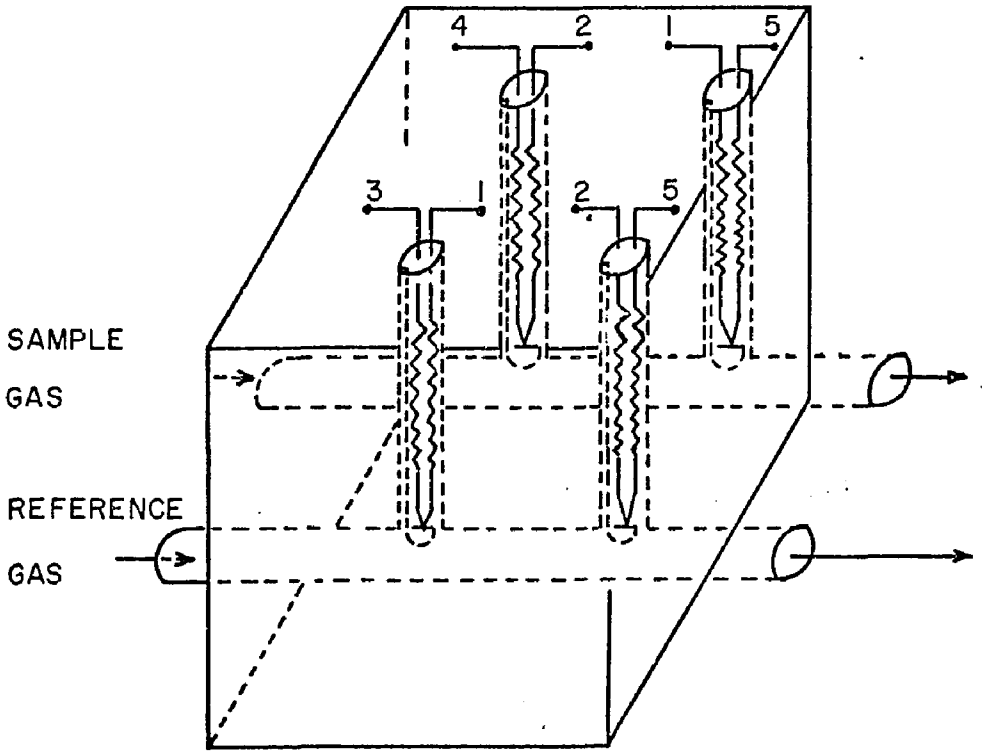


FIGURE-4. T.C. CELL.

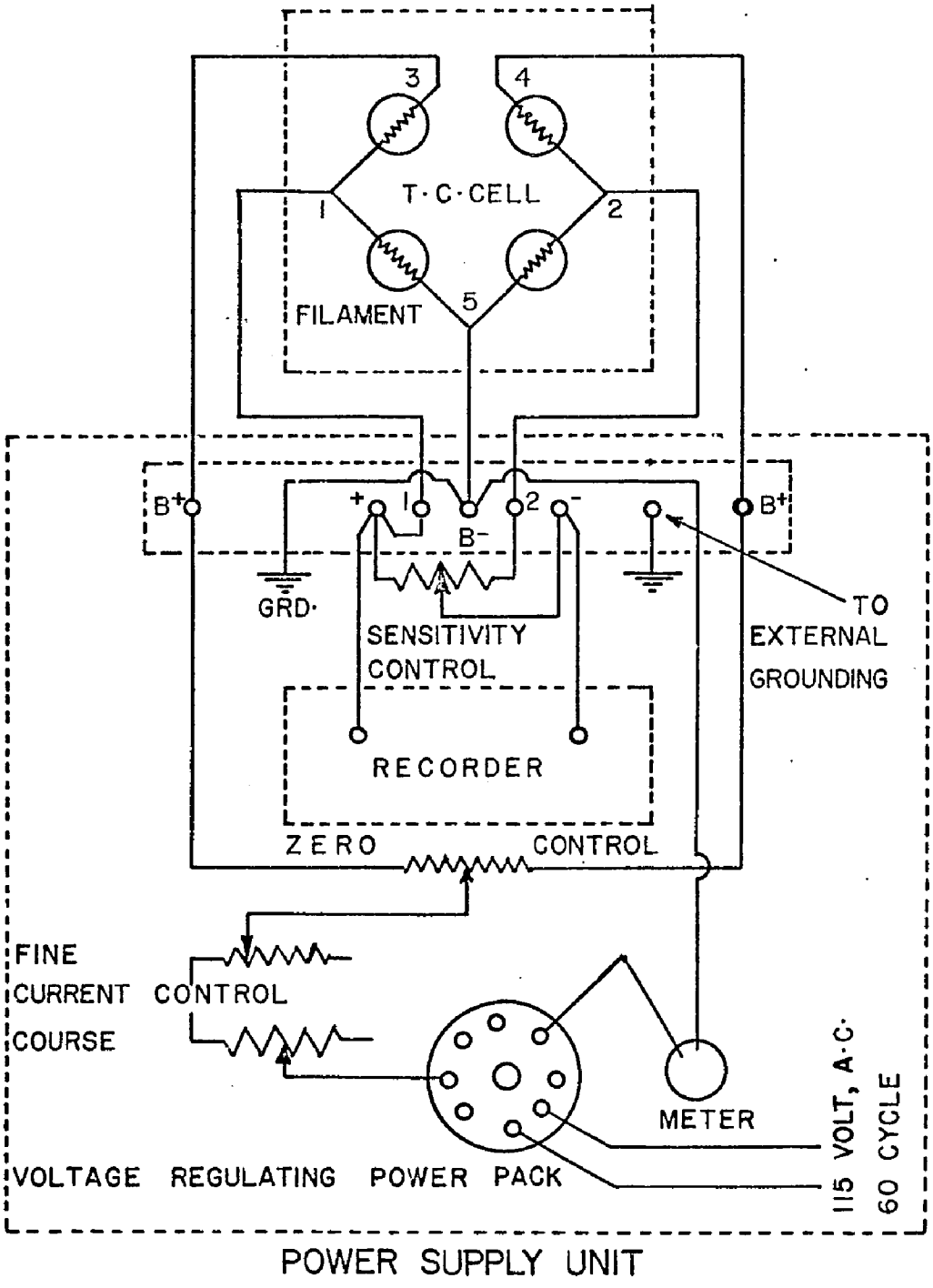


FIGURE-5. T.C.CELL WIRING DIAGRAM

(c) a Soap bubble flow meter, a number of rotameters

(d) two multipoint recorders and a portable recorder checker

(e) a number of cylinder pressure - and line pressure - regulators,

(f) a water-bath, and

(g) a constant temperature oven.

(b) PROCEDURE OF MEASUREMENT

The measurement of diffusion coefficients of binary gaseous systems using the present technique consisted of two stages of operation e.g.

(a) calibrations of T.C. Cells and Diffusion Cell, and

(b) measurement of diffusivity.

1. CALIBRATION OF THERMAL CONDUCTIVITY CELLS:

About 1000 ml/min. of gas 1 metered accurately in a rotameter was led into a mixing chamber and as the gas left the mixing chamber it was bleeded and only 100 ml/min. metered in a second rotameter was led into the sample side of the T.C. Cell-1. Through the reference side of the same T.C. Cell 100 ml/min. of pure gas 1 was led all the time. A predetermined rate of direct current led from a power supply unit to the electrical circuit of the T.C. Cell was maintained constant during the process of calibration.

Under the conditions of 100 ml/min. of gas 1 flowing through both the reference as well as sample side of the T.C. Cell, constant current, constant temperature and pressure, the output of the T.C. Cell was attinuated such that the recorder read zero millivolt.

After the zero had thus been established, gas 2 metered in a separate rotameter was led into the same mixing chamber and 100 ml/min. of

this mixture was led into the sample side of the T.C. Cell. The output was recorded in millivolts while the corresponding concentration of gas 2 in gas 1 was calculated from the known flow rates of the two gases.

The process was repeated for several flow rates of gas 2, keeping that of gas 1 constant, and a chart was prepared with concentration of 2 in 1 versus millivolt.

A similar chart was prepared for concentration of gas 1 in gas 2 versus millivolt using T.C. Cell-2 and employing the same procedure but interchanging the gases.

These charts were later used to obtain the concentration of gas streams after the diffusion had taken place.

2. CALIBRATION OF DIFFUSION CELL:

The conditions in the diffusion cell approached steady state counter diffusion and therefore Sherwood's solution[18A] of the Maxwell-diffusion equation could be employed for the calculation of the diffusion coefficients of binary gaseous systems provided the diffusion path and area were known or previously determined. Sherwood's equation after rearranging becomes:

$$D_{12} = \frac{N_1 \left(1 - \frac{N_2}{N_1}\right) RTz}{SP} \Big/ \log_e \frac{1 - \left(1 - \frac{N_2}{N_1}\right) y_{12}}{1 - \left(1 - \frac{N_2}{N_1}\right)\left(1 - y_{21}\right)} \qquad \text{Eq. 32}$$

where D_{12} is the true diffusivity of gas 1 in 2, $cm^2/sec.$,

N_1, N_2 are molar rates of diffusion or transport of 1 and 2 respectively, moles/sec.,

y_{12}, y_{21} are mole fractions of 1 in compartment 2 and of 2 in com-

partment 1 respectively,

R is the universal gas constant, (c.c.)(atm.)/(°K)(gm-mole),

T is temperature, °K,

P is the diffusion pressure, atm.,

z is the diffusion path, cm.,

S is the diffusion area, $cm.^2$.

Obviously for the calculation of D_{12} it is necessary to have a knowledge of total transport rate, $N_1 - N_2$, transport ratio, N_2/N_1, concentrations of the outgoing streams, y_{12} and y_{21}, temperature, T, pressure, P, diffusion path, z, and the diffusion area, S.

While it is possible to calculate z and S from a measurement of geometric length and area of the pores of the solid used as diffusion medium in the diffusion cell, such a measurement is not likely to give any indication of their dependence on temperature or any other variables involved in the process of diffusion. If, on the other hand, measurements of the rates of diffusion are carried out for any particular gas pair in such a diffusion cell employing a solid of certain specific material with certain specific nominal pore size under such conditions of temperature and pressure at which their true diffusion coefficients, D_{12}, are fairly accurately known, then a factor, γ, involving z/S can be determined experimentally. This diffusion cell calibration factor, γ, then becomes mathematically equal to the ratio of true diffusivity, D_{12}, to effective diffusivity, D_E, i.e. $\gamma = D_{12} / D_E$. The effective diffusivity is defined by the following equation:

$$D_E = \frac{N_1 \left(1 - \frac{N_2}{N_1}\right) RT}{P} \Bigg/ \log_e \frac{1 - \left(1 - \frac{N_2}{N_1}\right) y_{12}}{1 - \left(1 - \frac{N_2}{N_1}\right)\left(1 - y_{21}\right)} \qquad \text{Eq. 33}$$

The calculation of diffusion coefficient with the help of Eq. 32, further necessitates a previous knowledge of the total mass transport for counter flow, $N_1 - N_2$, as well as the ratio of the two transport rates, N_2/N_1.

The ratio of the two transport rates, N_2/N_1, for the case of constant pressure steady state diffusion, as shown by Hoogschagen[6], can be estimated by the following relationship:

$$\frac{N_2}{N_1} = \sqrt{\frac{M_1}{M_2}} \qquad \text{Eq. 34}$$

where M_1, M_2 are the respective molecular weights of 1 and 2.

The use of Eq. 34, however, requires the condition of the same constant pressure in the two compartments on the two sides of the porous solid within the diffusion cell. This is a difficult condition to achieve in practice. In the present work, therefore, this was avoided and both the total transport of mass, $N_1 - N_2$, and the ratio of the two transport rates, N_2/N_1, were calculated by actually measuring the concentrations in the two compartments and making a material balance around the diffusion cell.

The gas pairs selected for the purpose of calibration of the diffusion cell were Helium - Argon; Helium - Nitrogen, and Nitrogen - Carbon dioxide. These gas pairs are representative of monatomic - monatomic, monatomic - diatomic, and diatomic - triatomic molecular encounters and their true diffusion coefficients have been measured fairly accurately by Walker and Westenburg[20] employing the so-called point-source technique.

The procedure of calibration of diffusion cell thus involved that of the measurement of effective diffusivities of the above systems at

various temperatures.

3. MEASUREMENT OF EFFECTIVE DIFFUSION COEFFICIENT

Written in terms of measured variables Eq. 33 is reduced to the following operating equation:

$$D_E = \frac{(B_2 y_{12} - A_1 y_{21})}{(1 - y_{12} - y_{21})} \left(\frac{P_R T}{P_s T_R}\right) \Big/ 60 \log_e \left(\frac{B_2 y_{12}}{A_1 y_{21}}\right) \qquad \text{Eq. 35}$$

where A_1 = Volumetric flow rate of gas 1 into compartment 1 measured under the conditions of room temperature and barometric pressure, cc./min.

B_2 = Volumetric flow rate of gas 2 into compartment 2 measured also under the conditions of room temperature and barometric pressure, cc/min.

y_{12} = Concentration of gas 1 in the stream leaving the compartment 2, mole fraction.

y_{21} = Concentration of gas 2 in the stream leaving the compartment 1, mole fraction.

P_R, P_S = Reference and standard pressures respectively, atmospheres.

T_R, T = Reference and diffusion temperatures respectively, °K.

Flow rates A_1 and B_2 were metered in rotameter type flow meters and concentrations y_{12} and y_{21} were measured in previously calibrated thermal conductivity cells. P_R was the barometric pressure and P_S was taken as 1 atmosphere.

Room temperature, diffusion temperature, and thermal conductivity bath temperature were measured using copper-constantant thermocouples and

recorded in a multipint recorder.

The flow lines were so constructed that the pressure-drop in the lines were negligible. Under these conditions the diffusion pressure was the same as the reference pressure which in turn was the same as barometric pressure.

The results on diffusion cell calibration factor, γ, and on diffusion measurements of the systems whose diffusivities are unknown, are presented in the next section, RESULTS.

V. RESULTS

(a) RESULTS OF THE ANALYSIS OF EXPERIMENTALLY MEASURED DIFFUSION AND VISCOSITY DATA:

The generalized plot of

$$\left\{ \frac{0.0026280\ T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{PD_{12}} \right\}$$

versus

$$\left\{ \sigma_{12}^2\ \Omega^{(1,1)^*}_{(T_{12}^*)} \right\}_{L\text{-}J},$$

as shown in Figure - 6 and prepared with data of all the nonpolar - nonpolar systems that are available in the literature, gave a straight line with

slope, β = 0.9461,

intercept, α = - 0.0371

standard deviation, σ = $\pm$ 2.0619

and average deviation = 4.9%,

rather than the straight line passing through the origin and having a slope equal to unity which would be expected from Hirschfelder's prediction equation.

A similar plot, shown in Figure - 7, prepared with data of all nonpolar - polar systems, available in the literature, using Lennard-Jones potential parameters, gave a straight line with

slope, β = 1.0867

intercept, α = -0.8373

standard deviation, σ = $\pm$ 2.307 and average deviation = 12.7%.

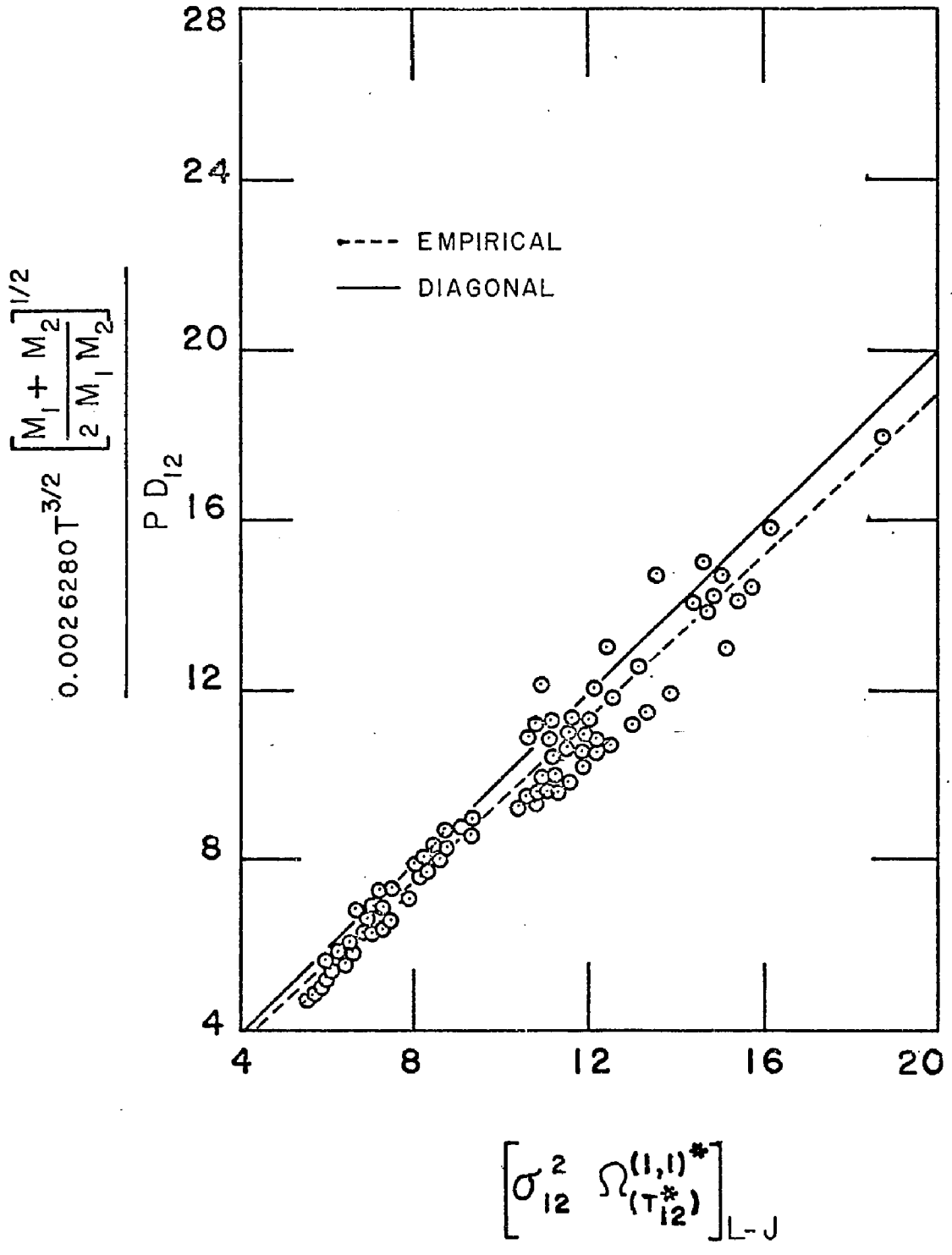
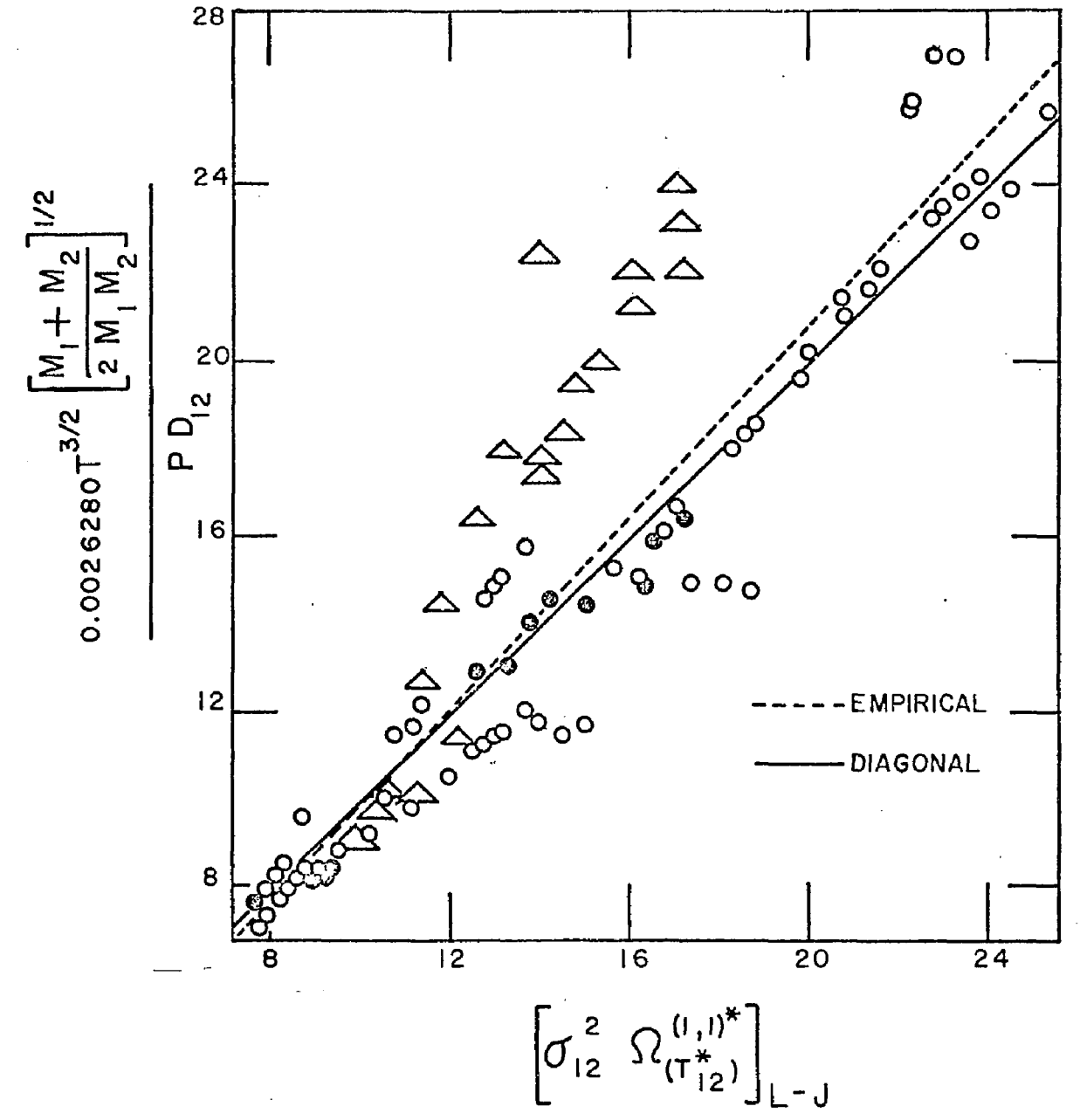


FIGURE-6. NONPOLAR-NONPOLAR SYSTEMS



● SYSTEMS INVOLVING NH_3 AS POLAR COMPONENT

○ SYSTEMS INVOLVING H_2O, CH_3OH, C_2H_5OH, ISOPROPYL ALCOHOL, ETHYL ACETATE, & CHLOROFORM AS THE POLAR COMPONENT

△ SYSTEMS INVOLVING CO, HCl, & SO_2 AS THE POLAR COMPONENT

FIGURE-7. NONPOLAR-POLAR SYSTEMS

Figure - 8 is another plot of

$$\left\{ \frac{0.0026280\ T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{PD_{12}} \right\}$$

versus

$$\left\{ \sigma_{np}^2\ \Omega^{(1,1)^*}_{(T_{np}^*)} \right\}_{STOCK.} ,$$

using Stockmayer's potential parameters rather than Lennard-Jones'. In this case also a straight line with slope, $\beta = 1.0329$

intercept, $\alpha = -0.3372$

standard deviation, $\sigma = \pm 2.437$

and average deviation = 13.02 %, was obtained.

Figure - 9, is a plot of

$$\log \left[\frac{0.0026280\ T^{3/2} \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{1/2}}{PD_{12}} \right]$$

versus

$$\log \left[\frac{\epsilon_{12}\ \sigma_{12}^2}{k\ T} \right]_{L\text{-}J} ,$$

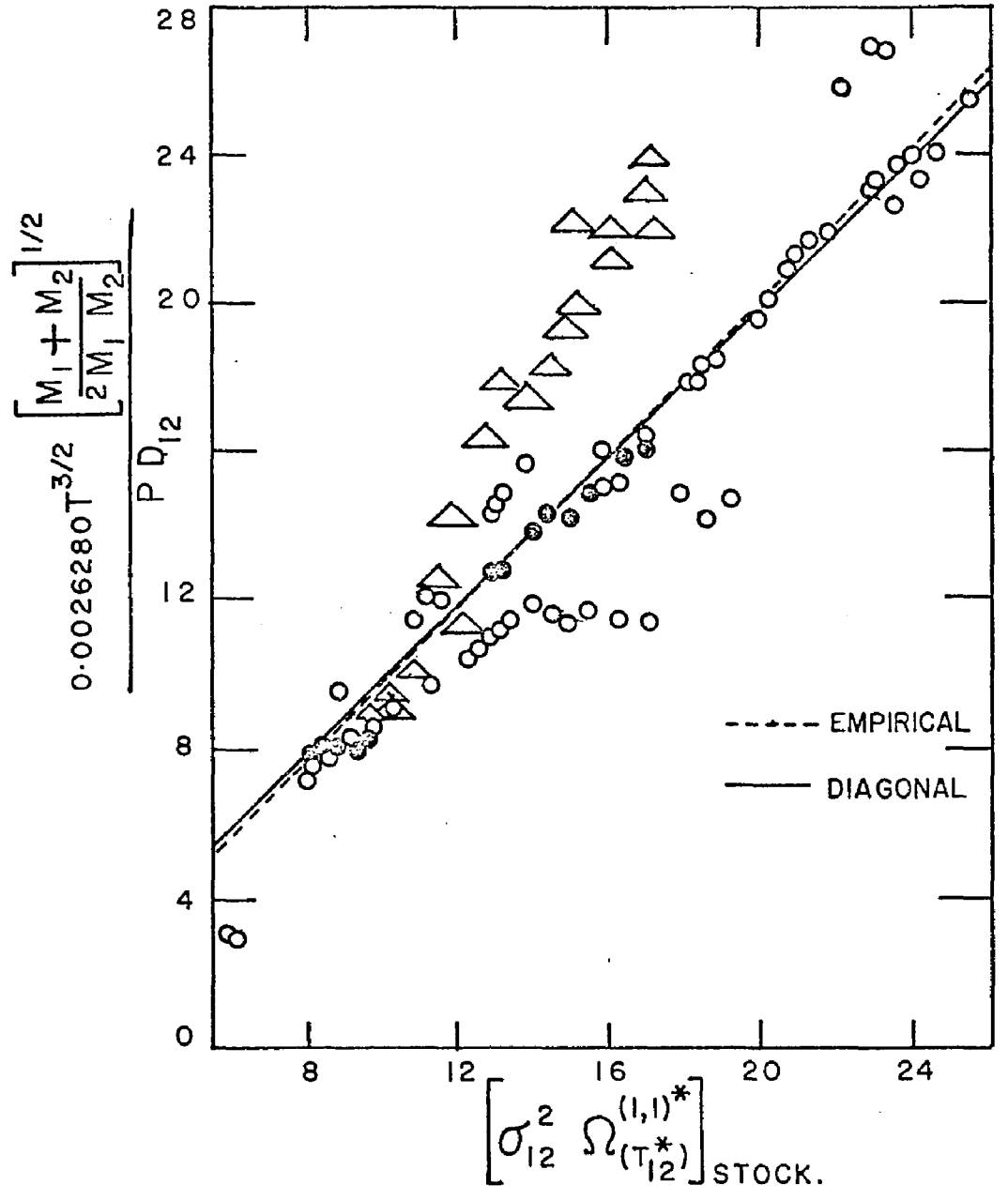
using Lennard-Jones potential parameters, and consisting of nonpolar-nonpolar systems. The best fitted curve was a straight line with

slope, $\beta = 0.2589$

intercept, $\alpha = 2.0055$

standard deviation, $\sigma = \pm 0.1865$ and average deviation equal to 5.3%.

Figure - 10, a similar plot, using Lennard-Jones potential parameters



● SYSTEMS INVOLVING NH_3 AS POLAR COMPONENT

o SYSTEMS INVOLVING H_2O, CH_3OH, C_2H_5OH, ISOPROPYL ALCOHOL, ETHYL ACETATE, & CHLOROFORM AS THE POLAR COMPONENT

△ SYSTEMS INVOLVING CO, HCl, & SO_2 AS THE POLAR COMPONENT

FIGURE - 8 · NONPOLAR - POLAR SYSTEMS

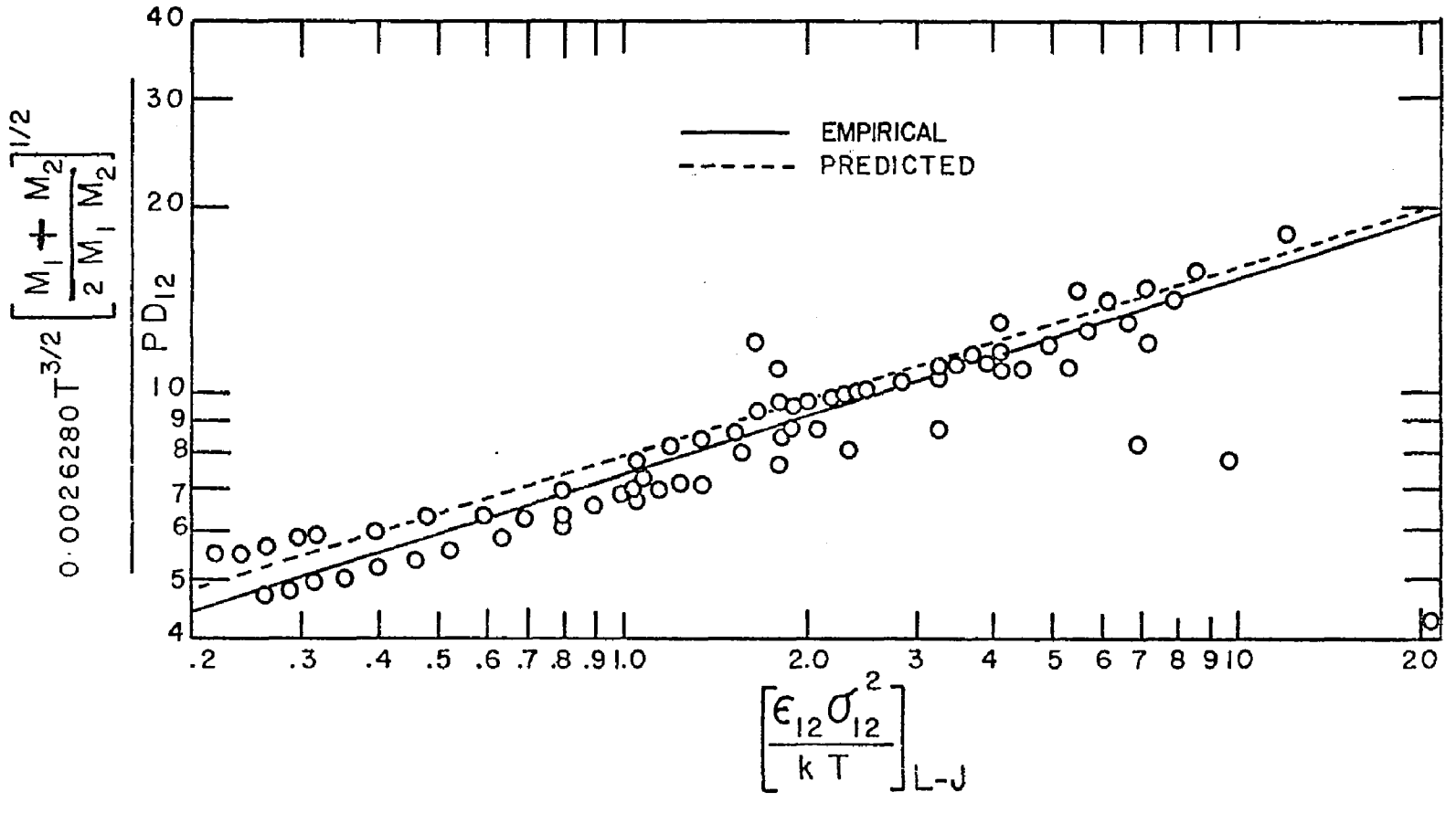
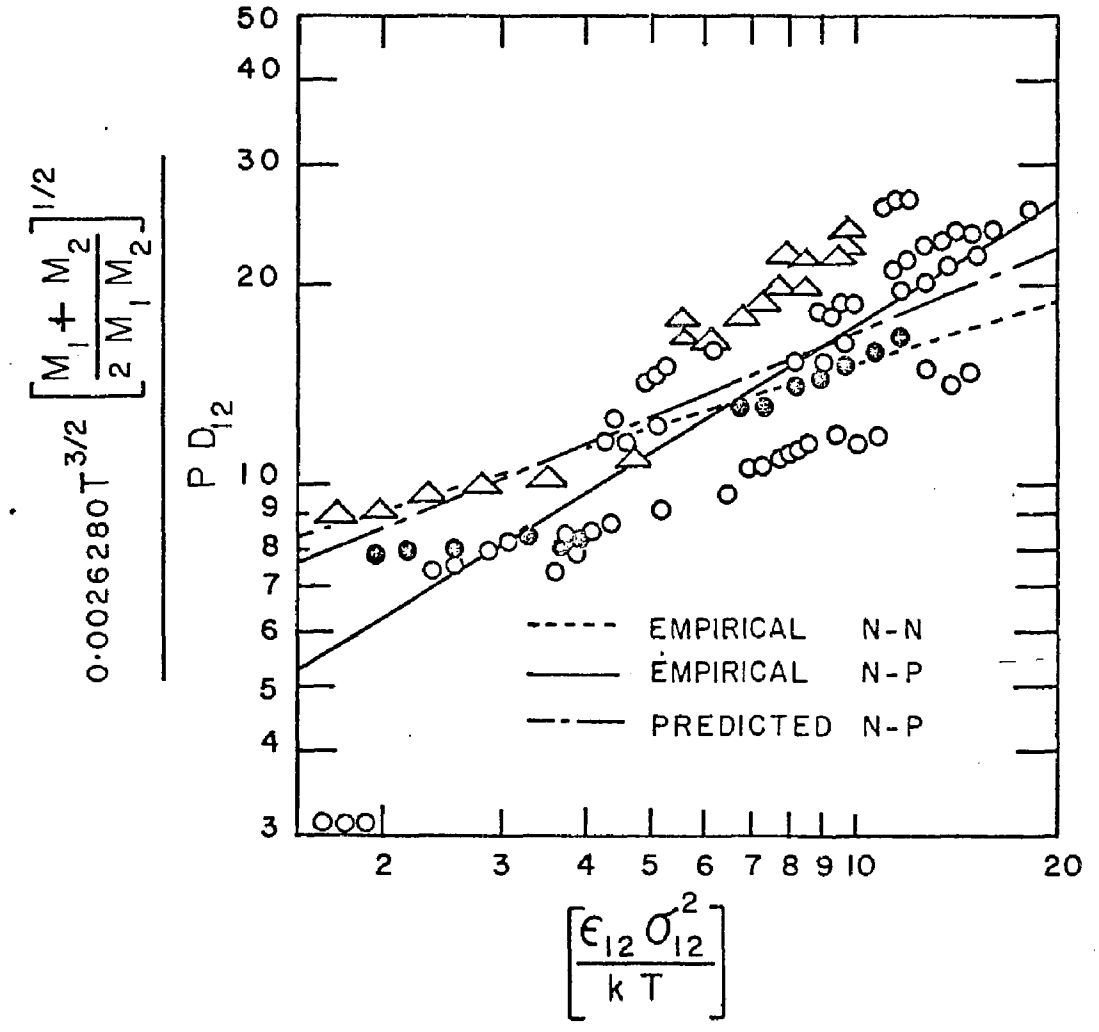


FIGURE - 9. NONPOLAR - NONPOLAR SYSTEMS



● SYSTEMS INVOLVING NH_3 AS POLAR COMPONENT

o SYSTEMS INVOLVING H_2O, CH_3OH, C_2H_5OH, ISOPROPYL ALCOHOL, ETHYL ACETATE, & CHLOROFORM AS THE POLAR COMPONENT

△ SYSTEMS INVOLVING CO, HCl, & SO AS THE POLAR COMPONENT

FIGURE-10· NONPOLAR-POLAR SYSTEMS

and consisting of nonpolar - polar systems, gave a straight line with

slope, $\beta = 0.6243$

intercept, $\alpha = 1.4242$

standard deviation, $\sigma = \pm 0.2537$, and average deviation equal to 8.97% while Figure - 11, using Stockmayer's potential parameters and consisting of nonpolar - polar systems, gave a straight line with

slope, $\beta = 0.621$

intercept, $\alpha = 1.4139$

standard deviation, $\sigma = \pm 0.2619$ and average deviation equal to 9.3%.

Figure - 12, is a log - log plot of collision integrals, $\Omega^{(2,2)*}_{(T^*)}$, for like molecular interactions, plotted against T^* for different values of δ_{max} prepared with values obtained by Mason and Monchick[11] while Figure - 13 is a similar plot of collision integrals, $\Omega^{(1,1)*}_{(T^*_{12})}$, for unlike molecular interactions, plotted against T^*_{12}.

Table - II gives the slopes,

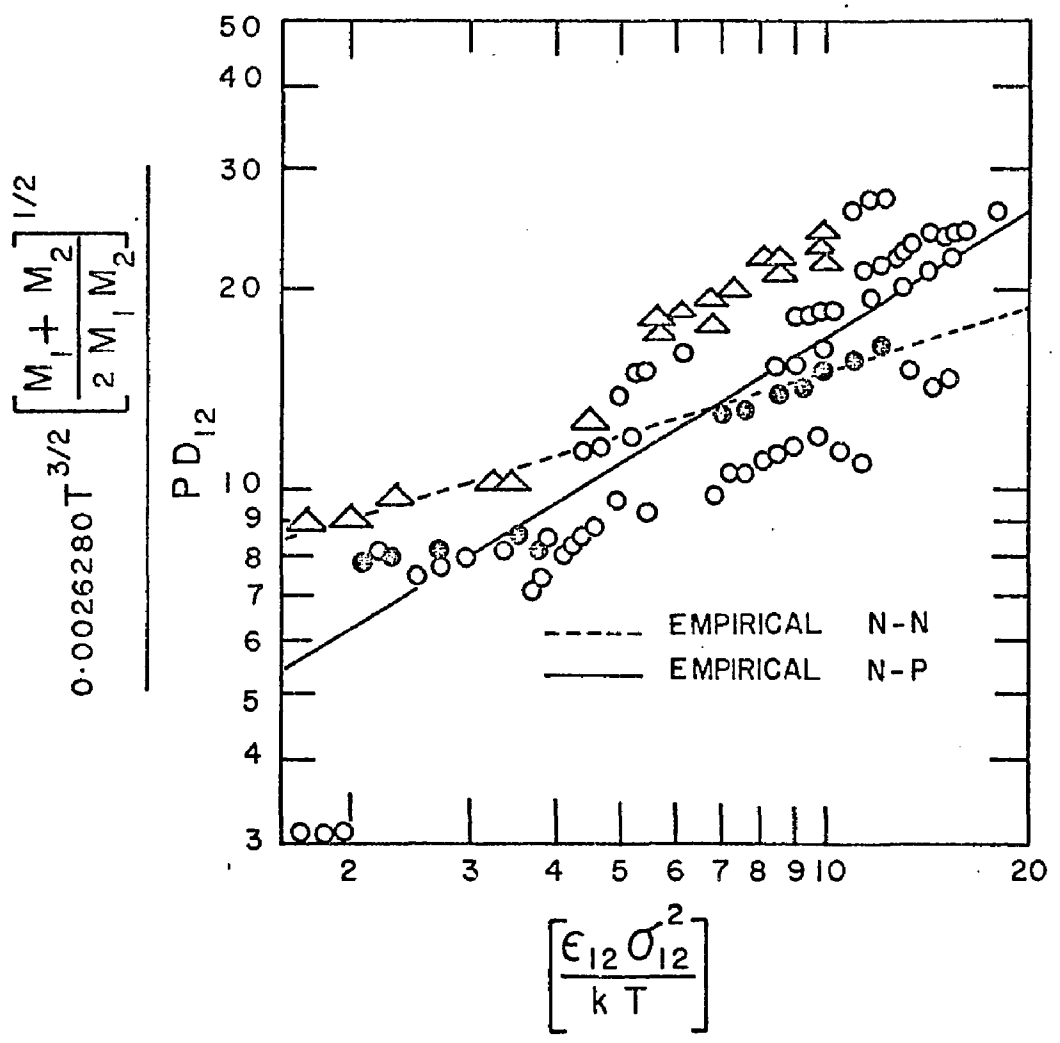
$$-m \left(= \frac{d \log \Omega^{(2,2)*}}{d \log T^*} \right) ,$$

obtained from figure - 12, as a function of T^*_{avg} for different values of δ_{max} while Table - II gives

$$-m \left(= \frac{d \log \Omega^{(1,1)*}}{d \log T^*_{12}} \right) ,$$

obtained from Figure - 13, as a function of $T^*_{12,avg}$ for various values of δ_{max}.

Figures 14 and 15 are graphical representations of Table - I and II respectively plotted on semi - log scale.



● SYSTEMS INVOLVING NH_3 AS POLAR COMPONENT

o SYSTEMS INVOLVING H_2O, CH_3OH, C_2H_5OH, ISOPROPYL ALCOHOL, ETHYL ACETATE, & CHLOROFORM AS THE POLAR COMPONENT

△ SYSTEMS INVOLVING CO, HCl, & SO AS THE POLAR COMPONENT

FIGURE-11· NONPOLAR-POLAR SYSTEMS

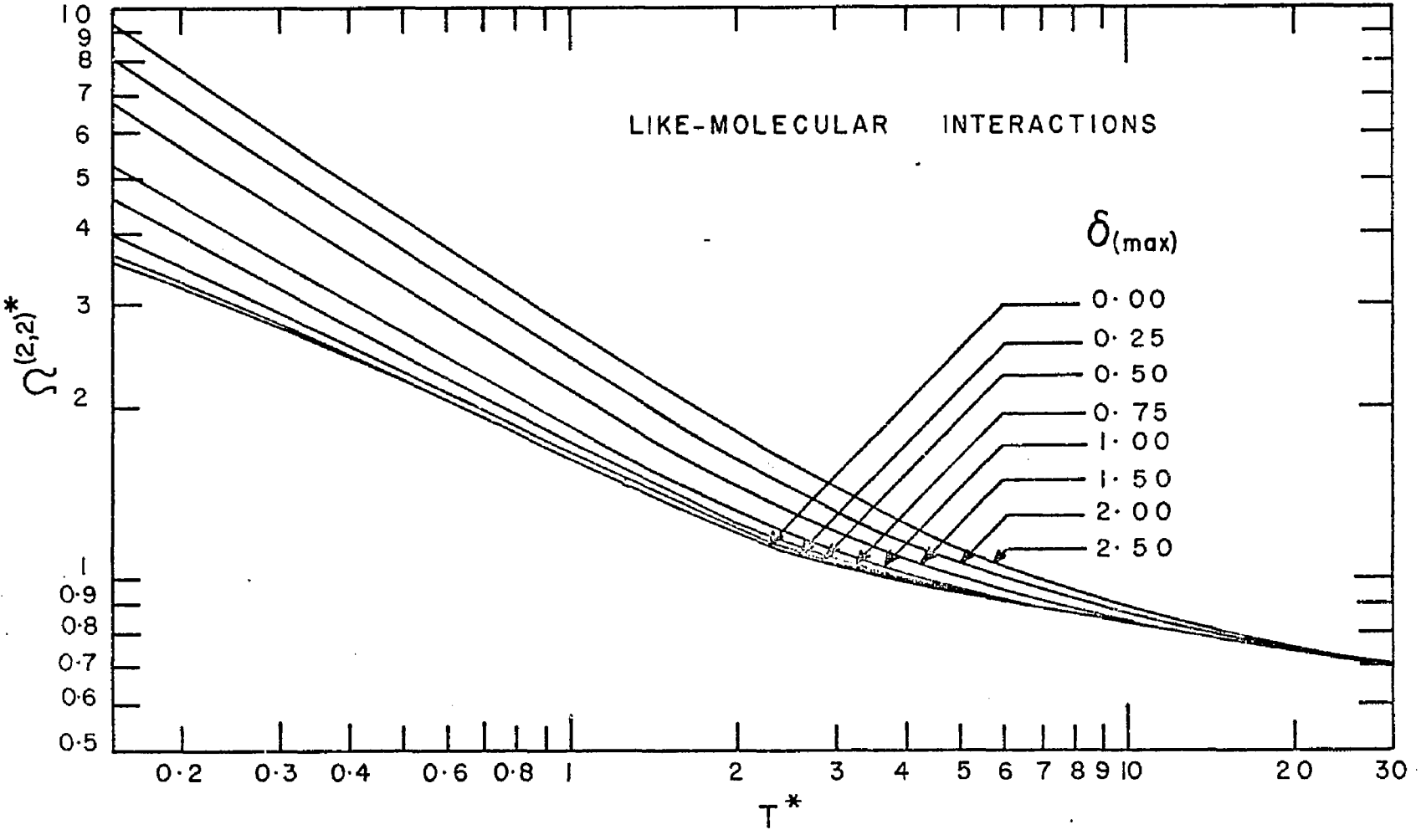


FIGURE - 12· $\Omega^{(2,2)*}$ VS T^*

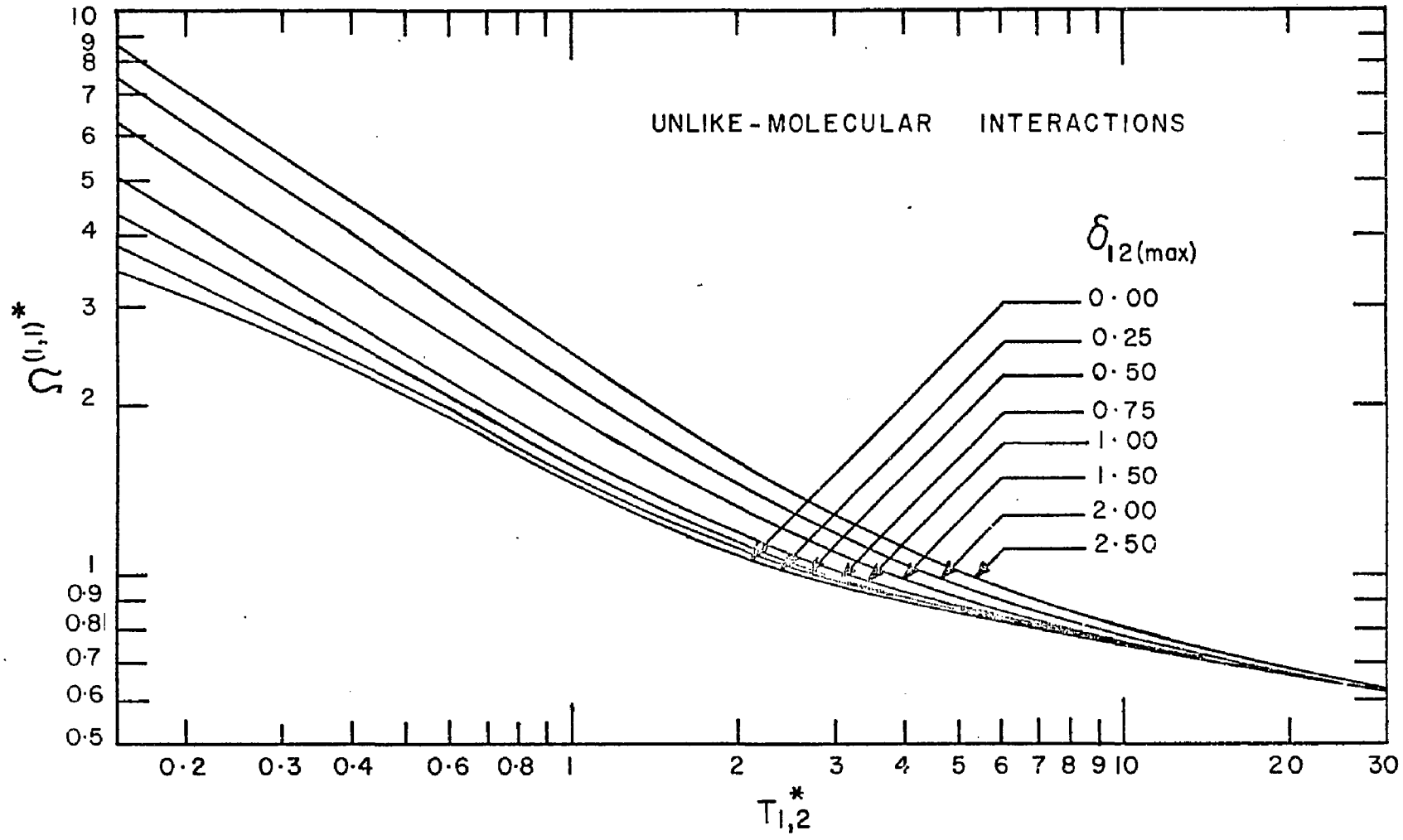


FIGURE - 13· $\Omega^{(1,1)*}$ VS $T^*_{1,2}$

TABLE - I

$$\frac{d(\log\ \Omega^{(2,2)^*})}{d(\log\ T^*\ )} = -m_{vis}$$

T^* \ $\delta_{max.}$	0.0000	0.2500	0.5000	0.7500	1.0000	1.5000	2.0000	2.5000
				$-m_{vis.}$				
0.15	0.3297	0.3682	0.4589	0.5529	0.6021	0.6306	0.6396	0.6422
0.25	0.3422	0.3774	0.4446	0.5215	0.5750	0.6216	0.6371	0.6411
0.35	0.4002	0.4078	0.4412	0.4931	0.5421	0.6025	0.6253	0.6337
0.45	0.4607	0.4579	0.4690	0.4977	0.5366	0.5955	0.6220	0.6342
0.55	0.5024	0.4936	0.4898	0.5065	0.5357	0.5861	0.6194	0.6328
0.65	0.5243	0.5088	0.5065	0.5144	0.5369	0.5925	0.6147	0.6311
0.75	0.5320	0.5197	0.5112	0.5161	0.5407	0.5867	0.6184	0.6343
0.85	0.5277	0.5167	0.5086	0.5158	0.5331	0.5777	0.6057	0.6221
0.95	0.5182	0.5078	0.5003	0.5088	0.5321	0.5806	0.6076	0.6252
1.10	0.4962	0.4869	0.4881	0.5024	0.5257	0.5738	0.6042	0.6233
1.30	0.4618	0.4586	0.4648	0.4832	0.5088	0.5629	0.5978	0.6188
1.50	0.4269	0.4290	0.4349	0.4597	0.4859	0.5490	0.5912	0.6126
1.70	0.3943	0.3908	0.4081	0.4309	0.4642	0.5264	0.5732	0.6040
1.90	0.3658	0.3694	0.3846	0.4083	0.4468	0.5155	0.5691	0.5993
2.25	0.3256	0.3297	0.3466	0.3772	0.4089	0.4786	0.5378	0.5774
2.75	0.2804	0.2865	0.3022	0.3292	0.3610	0.4376	0.4998	0.5478
3.25	0.2493	0.2534	0.2689	0.2940	0.3275	0.3942	0.4617	0.5150
3.75	0.2262	0.2333	0.2472	0.2643	0.2948	0.3657	0.4229	0.4867
4.50	0.2038	0.2078	0.2195	0.2385	0.2630	0.3183	0.3853	0.4376
5.50	0.1841	0.1873	0.1968	0.2119	0.2315	0.2827	0.3339	0.3903
6.50	0.1719	0.1742	0.1821	0.1943	0.2107	0.2522	0.3000	0.3491
7.50	0.1642	0.1663	0.1725	0.1825	0.1970	0.2319	0.2736	0.0387
8.50	0.1589	0.1614	0.1658	0.1748	0.1854	0.2154	0.2529	0.6097
9.50	0.1553	0.1562	0.1603	0.1675	0.1789	0.2045	0.2366	0.2722
11.00	0.1518	0.1530	0.1573	0.1628	0.1699	0.1918	0.2186	0.2502
13.00	0.1490	0.1504	0.1526	0.1571	0.1638	0.1804	0.2023	0.2266
15.00	0.1475	0.1475	0.1502	0.1537	0.1590	0.1728	0.1905	0.2118
17.00	0.1466	0.1481	0.1491	0.1521	0.1562	0.1672	0.1819	0.2001
19.00	0.1461	0.1468	0.1479	0.1515	0.1537	0.1628	0.1764	0.1905
22.50	0.1458	0.1457	0.1474	0.1491	0.1519	0.1590	0.1689	0.1831
27.50	0.1455	0.1458	0.1465	0.1480	0.1501	0.1557	0.1626	0.1700
32.50	0.1452	0.1459	0.1459	0.1476	0.1484	0.1527	0.1586	0.1662
37.50	0.1448	0.1444	0.1455	0.1465	0.1475	0.1516	0.1567	0.1616
45.00	0.1444	0.1449	0.1449	0.1455	0.1468	0.1492	0.1537	0.1600
62.50	0.1443	0.1439	0.1438	0.1434	0.1437	0.1464	0.1501	0.1551
87.50	0.1460	0.1456	0.1438	0.1414	0.1407	0.1425	0.1460	0.1514

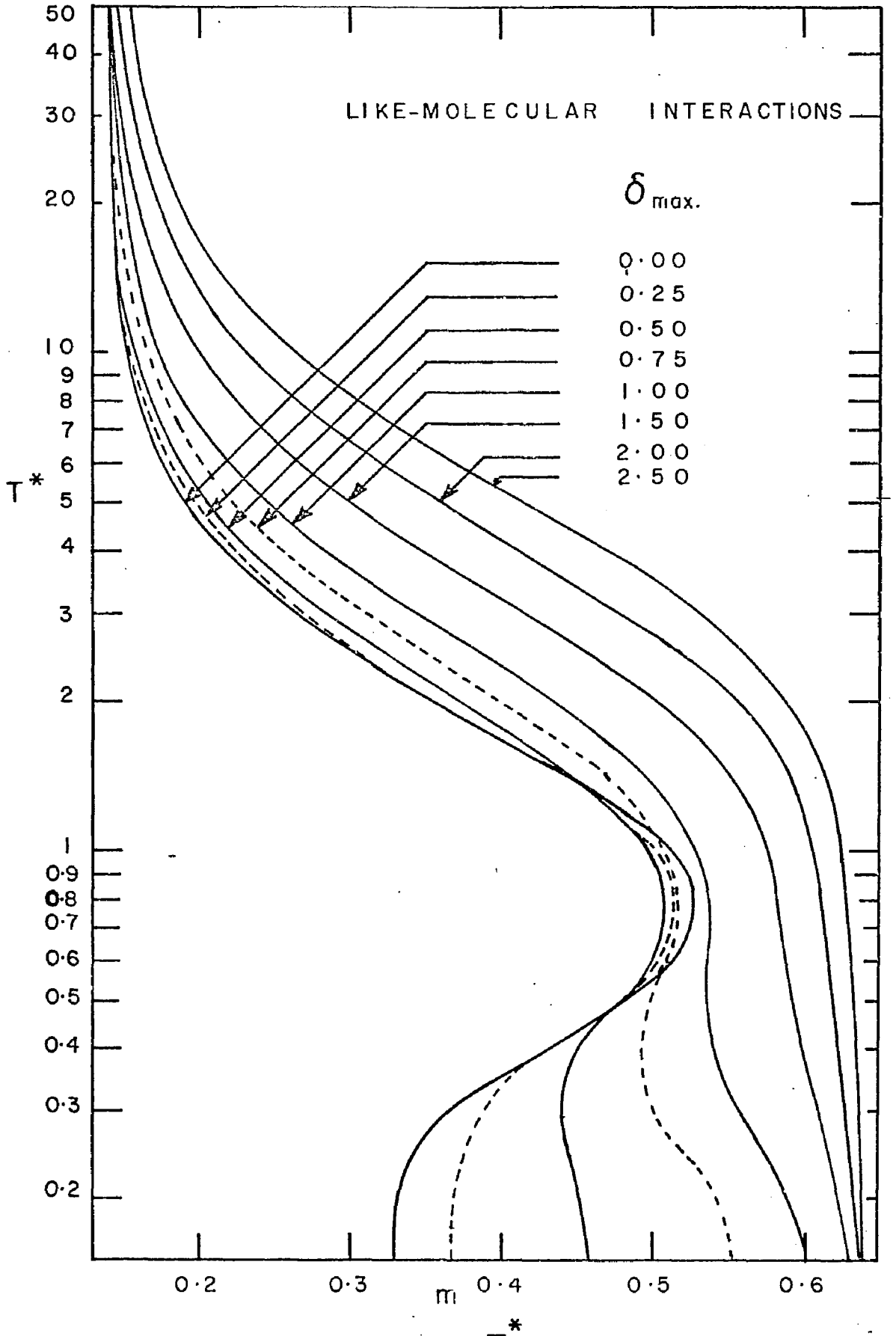


FIGURE - 14· T^* VS m

TABLE - II

$$\frac{d(\log \Omega^{(1,1)*})}{d(\log T^{*}_{12})} = -m_{diff.}$$

T^{*}_{12} \ δ_{max}	0.0000	0.2500	0.5000	0.7500	1.0000	1.5000	2.0000	2.5000
				$-m_{diff.}$				
0.15	0.3566	0.3389	0.4724	0.5692	0.6204	0.6512	0.6582	0.6595
0.25	0.4111	0.4307	0.4725	0.5295	0.5794	0.6281	0.6488	0.6581
0.35	0.4699	0.4714	0.4954	0.5373	0.5762	0.6258	0.6472	0.6567
0.45	0.5085	0.5044	0.5175	0.5439	0.5775	0.6238	0.6483	0.6593
0.55	0.5273	0.5214	0.5268	0.5517	0.5773	0.6265	0.6480	0.6596
0.65	0.5306	0.5267	0.5317	0.5484	0.5758	0.6212	0.6495	0.6619
0.75	0.5250	0.5172	0.5238	0.5455	0.5731	0.6208	0.6449	0.6609
0.85	0.5139	0.5124	0.5134	0.5325	0.5629	0.6167	0.6469	0.6606
0.95	0.4988	0.4910	0.5084	0.5252	0.5535	0.6088	0.6392	0.6619
1.10	0.4748	0.4738	0.4846	0.5104	0.5395	0.5947	0.6347	0.6551
1.30	0.4411	0.4440	0.4530	0.4768	0.5142	0.5795	0.6226	0.6478
1.50	0.4098	0.4089	0.4238	0.4547	0.4883	0.5531	0.6054	0.6399
1.70	0.3813	0.3839	0.4050	0.4261	0.4608	0.5336	0.5842	0.6216
1.90	0.3577	0.3614	0.3715	0.4091	0.4397	0.5116	0.5688	0.6118
2.25	0.3226	0.3308	0.3465	0.3659	0.4006	0.4721	0.5379	0.5855
2.75	0.2844	0.2867	0.3006	0.3284	0.3566	0.4288	0.4936	0.5443
3.25	0.2571	0.2609	0.2744	0.2957	0.3246	0.3891	0.4483	0.5064
3.75	0.2381	0.2417	0.2534	0.2730	0.2967	0.3528	0.4167	0.4756
4.50	0.2167	0.2200	0.2296	0.2455	0.2674	0.3190	0.3747	0.4261
5.50	0.1981	0.2010	0.2091	0.2221	0.2392	0.2828	0.3313	0.3798
6.50	0.1871	0.1891	0.1955	0.2060	0.2198	0.2562	0.2981	0.3431
7.50	0.1789	0.1801	0.1862	0.1945	0.2070	0.2374	0.2746	0.3132
8.50	0.1732	0.1755	0.1783	0.1862	0.1959	0.2223	0.2548	0.2904
9.50	0.1689	0.1696	0.1742	0.1811	0.1900	0.2128	0.2410	0.2727
11.00	0.1648	0.1664	0.1690	0.1744	0.1810	0.1999	0.2246	0.2517
13.00	0.1612	0.1613	0.1647	0.1688	0.1745	0.1897	0.2084	0.2311
15.00	0.1592	0.1604	0.1623	0.1652	0.1701	0.1825	0.1973	0.2154
17.00	0.1577	0.1581	0.1592	0.1627	0.1660	0.1760	0.1902	0.2062
19.00	0.1566	0.1573	0.1585	0.1597	0.1636	0.1725	0.1837	0.1985
22.50	0.1558	0.1558	0.1577	0.1589	0.1614	0.1682	0.1773	0.1881
27.50	0.1549	0.1552	0.1551	0.1576	0.1591	0.1638	0.1708	0.1792
32.50	0.1545	0.1547	0.1557	0.1567	0.1576	0.1624	0.1671	0.1736
37.50	0.1543	0.1553	0.1552	0.1552	0.1575	0.1597	0.1642	0.1686
45.00	0.1539	0.1536	0.1543	0.1550	0.1557	0.1585	0.1620	0.1661
62.50	0.1536	0.1536	0.1535	0.1544	0.1543	0.1560	0.1589	0.1621
87.50	0.1537	0.1535	0.1535	0.1521	0.1534	0.1547	0.1559	0.1585

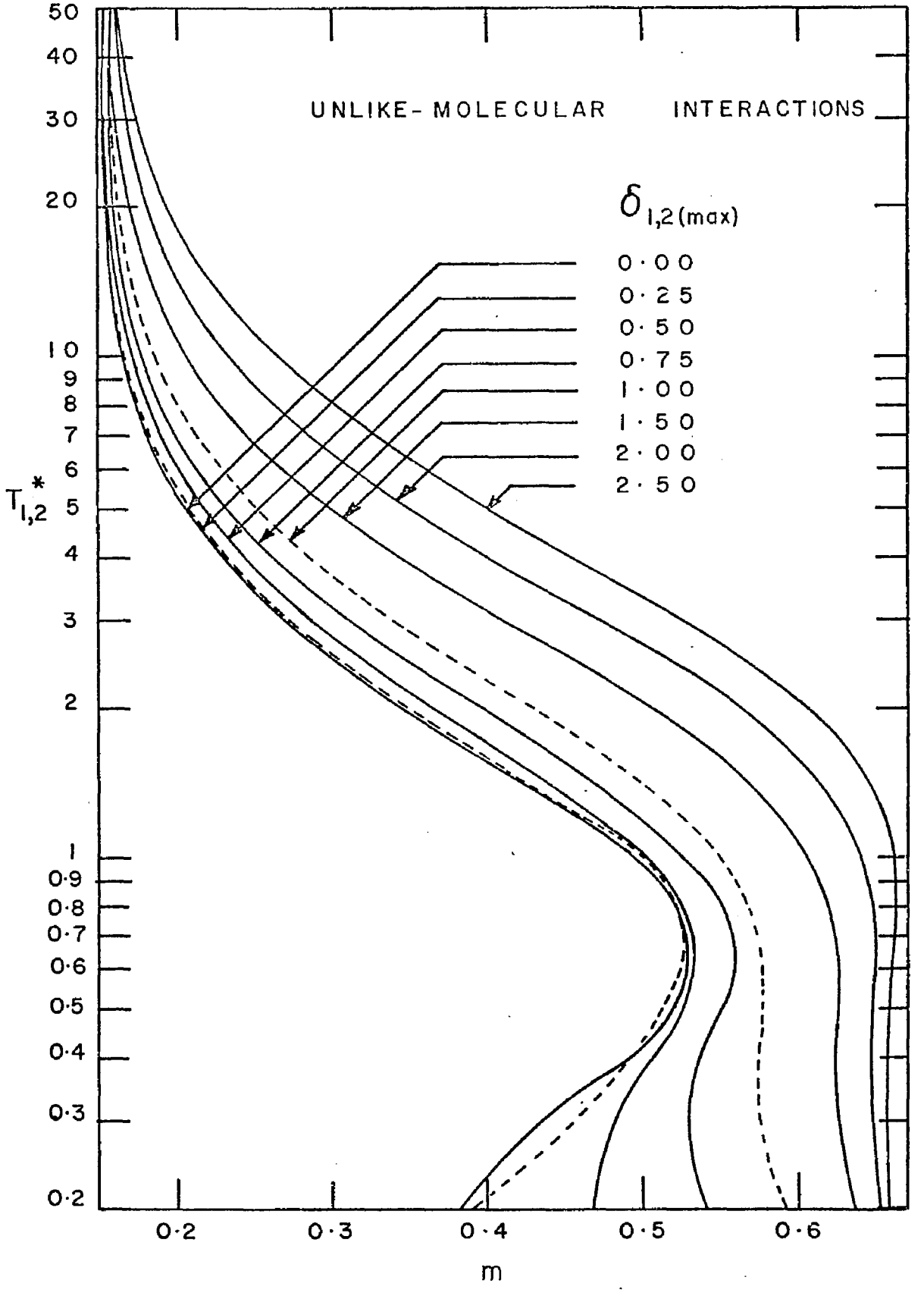


FIGURE-15· $T^*_{1,2}$ VS m.

Table - III compares the (12-6) potential parameters, ϵ/k and σ, obtained by the present direct method with those obtained by graphical technique, while Table - IV compares the (12-6-3) potential parameters, ϵ/k, σ, and δ_{max}, obtained from pure component viscosity data using the above techniques.

Tables - V and VI give the combined (12-6) potential parameters $\frac{\epsilon_{12}}{k}$, and σ_{12}, derived from diffusion data by the present direct method.

Figure - 16 is a plot of $\log \frac{\epsilon_{12}}{k}$ versus $\log \left[\frac{\epsilon_1}{k} \cdot \frac{\epsilon_2}{k} \right]$ while Figure - 17 is a plot of σ_{12} versus $(\sigma_1 + \sigma_2)$, for nonpolar - nonpolar systems. Figures - 18 and 19 are similar plots for nonpolar - polar systems assuming both components follow (12-6) potential functions in like molecular interactions in their respective pure states and also in the polar - nonpolar molecular interactions. Figures - 20 and 21 are also similar plots for nonpolar - polar systems assuming that the nonpolar component follows (12-6) potential in its pure state while the polar component follows (12-6-3) potential in its pure state and that the nonpolar - polar interaction follows (12-6) potential function.

TABLE - III

(12 - 6) Potential Parameters
derived from Viscosity data (5)

Systems	Direct method		Graphical method!	
	ϵ/k	σ	ϵ/k	σ
Helium	115.54	2.124	-----	-----
Argon	163.49	3.345	-----	-----
*Neon	6.87	3.154	27.50	2.858
Kyrpton	374.21	3.034	-----	-----
Xenon	252.55	3.329	-----	-----
Hydrogen	114.28	2.671	-----	-----
Nitrogen	101.63	3.680	-----	-----
Oxygen	146.31	3.379	-----	-----
Air	132.37	3.522	-----	-----
CH_4	180.23	3.690	144.00	3.796
C_2H_4	265.44	4.029	-----	-----
CO	95.72	3.669	-----	-----
CO_2	297.09	3.707	-----	-----
CH_3OH	126.66	4.557	452.00	3.666
C_2H_5OH	408.13	4.400	415.00	4.370
$i\text{-}C_3H_7OH$	215.56	5.618	-----	-----
$CH_3COOC_2H_5$	505.88	5.225	531.00	5.163
$CHCl_3$	347.08	5.360	327.00	5.430
HCl	323.10	3.396	360.00	3.305
HBr	391.31	3.001	-----	-----
HI	544.00	3.367	324.00	4.123
SO_2	439.12	3.884	363.00	4.026
H_2O	697.55	3.630	-----	-----
NH_3	564.21	3.302	-----	-----

! Values of parameters under Graphical method were taken from Mason and Monchick's work(11).

* Viscosity data of Neon did not fit the (12-6) potential function and consequently the maximum (-m) obtainable from (12-6) potential was used in deriving the parameters.

TABLE - IV

(12-6-3) Potential Parameters
derived from Viscosity data (5).

Systems	Direct Method			Graphical Method		
	$\delta_{max.}$	ϵ/k	σ	$\delta_{max.}$	ϵ/k	σ
CO	0.020	91.47	3.688	------	------	-----
CH_3OH	1.980	47.17	4.874	0.500	417.00	3.690
C_2H_5OH	0.280	542.63	4.106	0.300	431.00	4.310
$i\text{-}C_3H_7OH$	0.280	213.46	5.593	0.200	518.00	4.640
$CH_3COOC_2H_5$	0.012	505.88	5.248	0.160	499.00	5.240
$CHCl_3$	0.080	304.94	5.495	0.070	355.00	5.310
HCl	0.330	406.86	3.181	0.340	328.00	3.360
HBr	0.070	391.31	3.009	0.140	417.00	3.410
HI	0.250	544.00	3.373	0.029	313.00	4.130
SO_2	0.370	462.64	3.807	0.420	347.00	4.040
H_2O	1.000	653.95	3.437	1.000	775.00	2.520
NH_3	0.300	522.42	3.353	0.700	358.00	3.150

TABLE - V

(12 - 6) Potential Parameters
derived from diffusion data
(Ref. 1;9;10;12;15;17;18;19).

Systems	ϵ_{12}/k	σ_{12}
Nonpolar - Nonpolar		
Argon - Helium	207.68	2.412
Argon - Neon	125.11	2.752
Argon - Xenon	160.87	3.716
Argon - Nitrogen	94.60	3.494
Helium - Nitrogen	63.64	2.846
Hydrogen - Nitrogen	71.07	3.198
Hydrogen - Oxygen	250.00	2.617
*Hydrogen - Carbon dioxide	2.80	4.639
*Nitrogen - Carbon dioxide	7.50	4.571
Oxygen - Carbon dioxide	301.72	3.221
Osygen - Methane	391.57	3.012
*Argon - Helium	3.11	3.643
*Air - Helium	3.11	3.735
*Helium - Carbon dioxide	3.11	4.000
*Air - Carbon dioxide	2.97	5.248
*Carbon dioxide - Argon	2.97	5.194

* Systems marked with asterisk did not fit in (12-6) potential and consequently the maximum (-m) obtainable from (12-6) potential were used to derive the parameters.

TABLE - VI

(12 - 6) Potential Parameters
derived from diffusion data
(Ref. 1;10;12;15;17;18;19)

Systems	ϵ_{12}/k	σ_{12}
Polar - Nonpolar		
H_2O - O_2	243.51	2.971
H_2O - Air	249.38	2.965
H_2O - H_2	521.42	2.119
*NH_3 - H_2	4.03	3.957
NH_3 - A	262.37	3.149
NH_3 - Kr	341.69	3.131
*H_2O - He	3.30	2.454
*H_2O - CH_4	3.30	4.753
*H_2O - C_2H_4	3.30	5.329
CH_3OH - H_2	128.28	3.390
CH_3OH - Air	173.20	3.709
CH_3OH - CO_2	496.00	3.364
C_2H_5OH - H_2	158.83	3.749
C_2H_5OH - Air	227.07	3.891
C_2H_5OH - CO_2	212.88	4.470
i-C_3H_7OH - Air	213.18	4.236
$CH_3COOC_2H_5$ - Air	309.31	4.050
$CHCl_3$ - Air	187.80	4.823
CO - O_2	123.60	3.382
SO_2 - A	483.10	3.575
*HCl - A	683.33	2.923

* Systems marked with asterisk did not fit in 12-6 potential and consequently the maximum (- m) obtainable from that potential were used to derive the parameters.

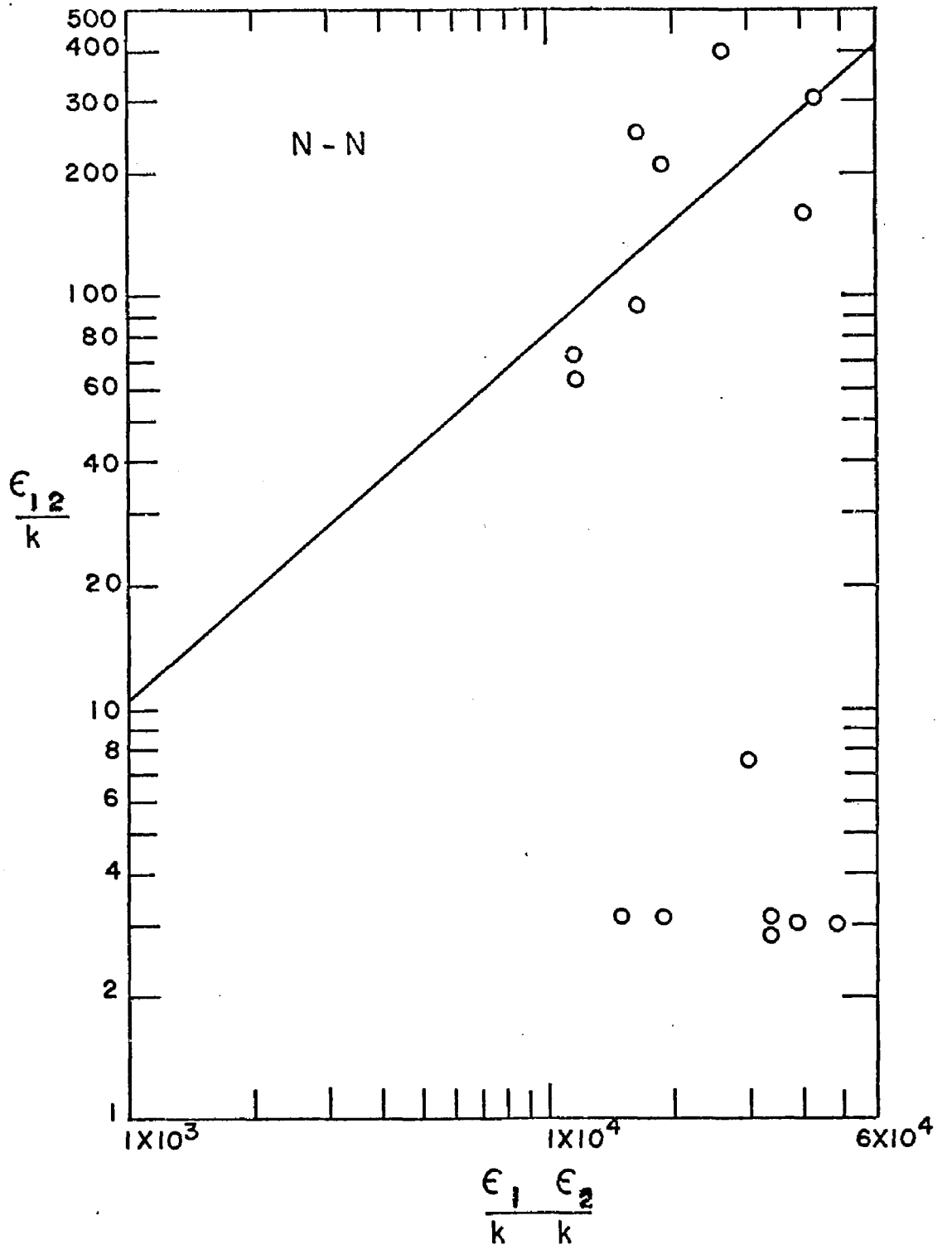


FIGURE - 16. $\left[\frac{\epsilon_{12}}{k}\right]_{\text{DIFF.}}$ VS $\left[\frac{\epsilon_1}{k}\ \frac{\epsilon_2}{k}\right]_{\text{VISC.}}$

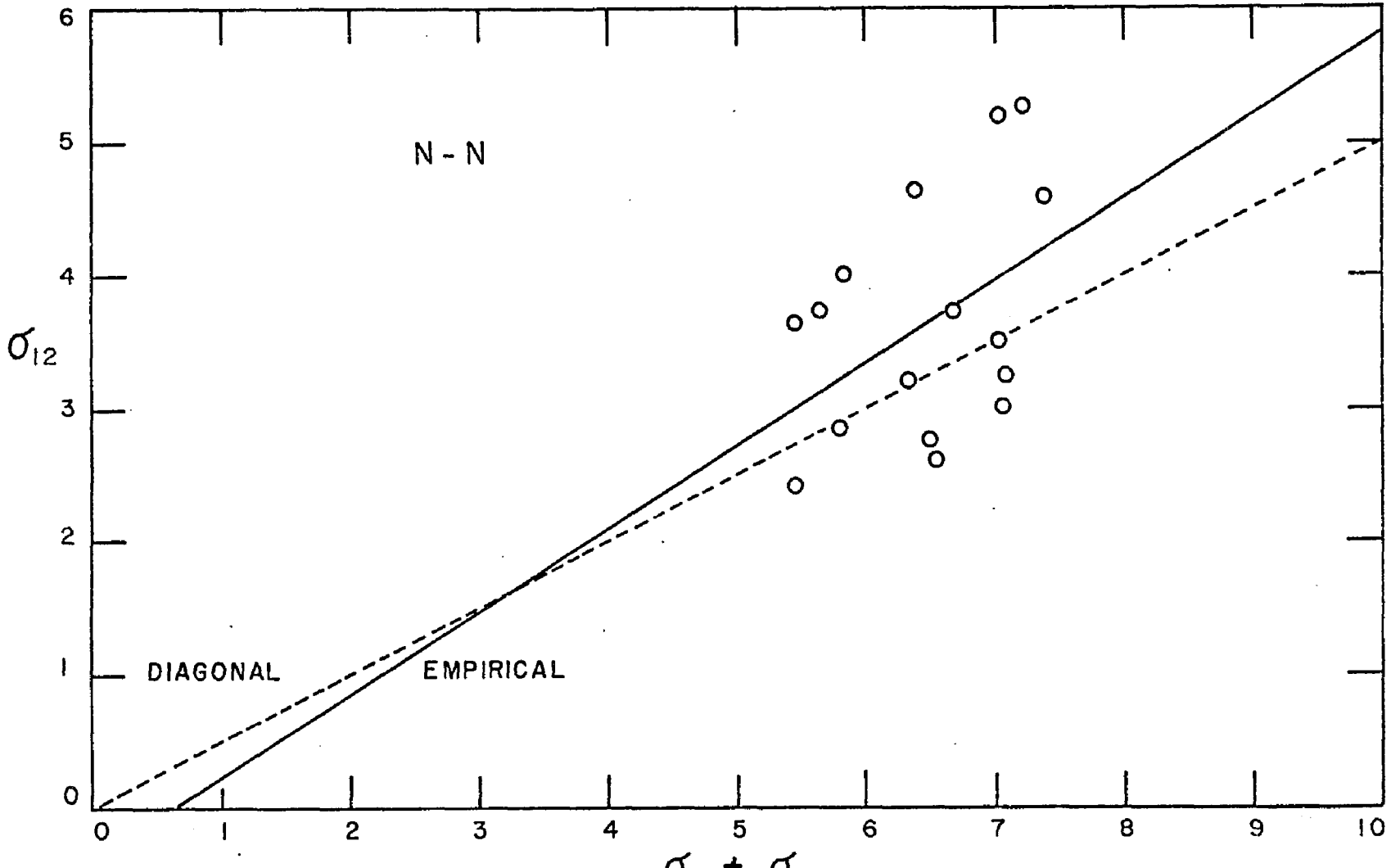


FIGURE - 17. $\left[\sigma_{12}\right]_{DIFF.}$ VS $\left[\sigma_1 + \sigma_2\right]_{VISC.}$

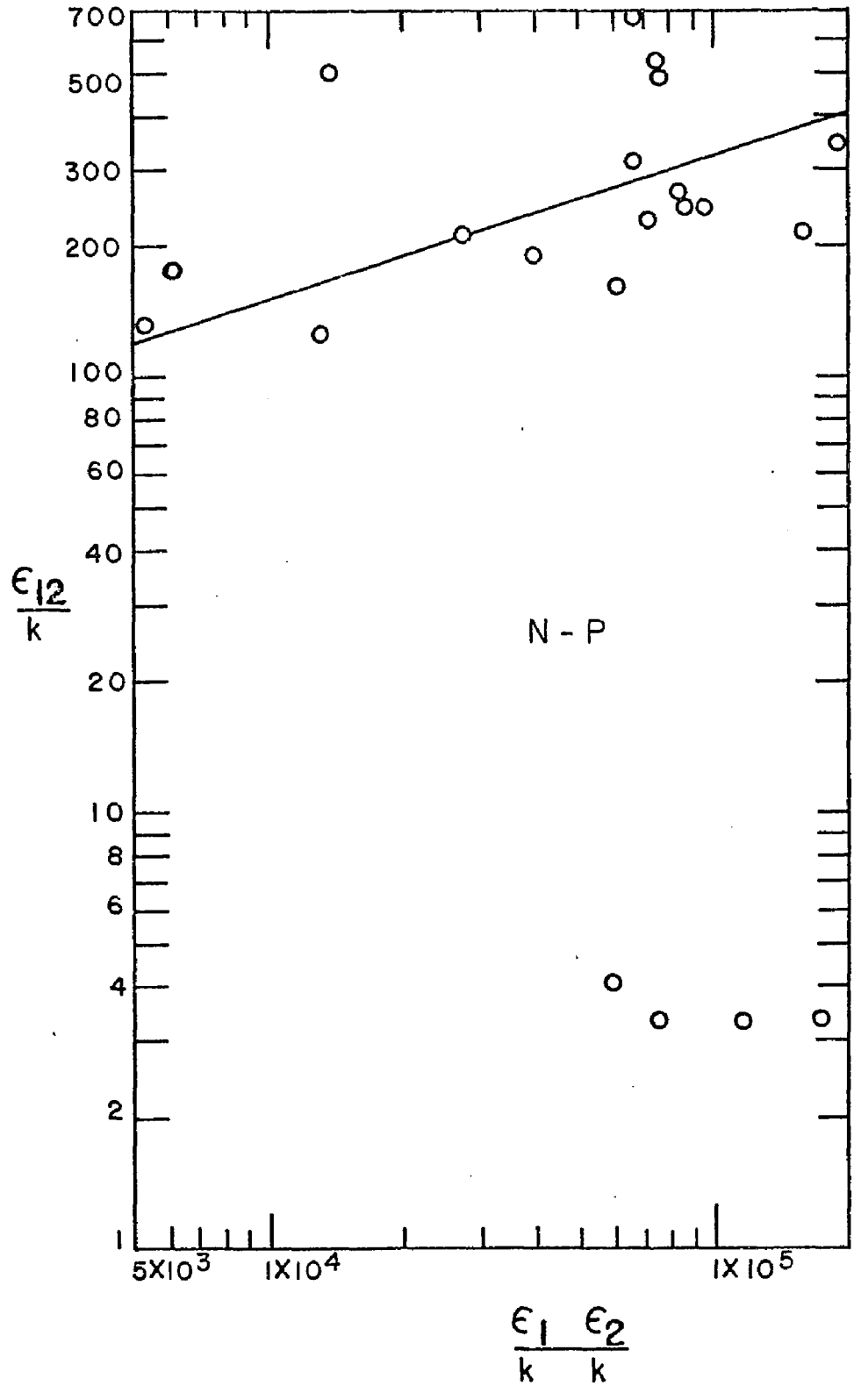


FIGURE - 18 · $\left[\frac{\epsilon_{12}}{k}\right]$ DIFF. VS $\left[\frac{\epsilon_1}{k}\ \frac{\epsilon_2}{k}\right]$ VISC.

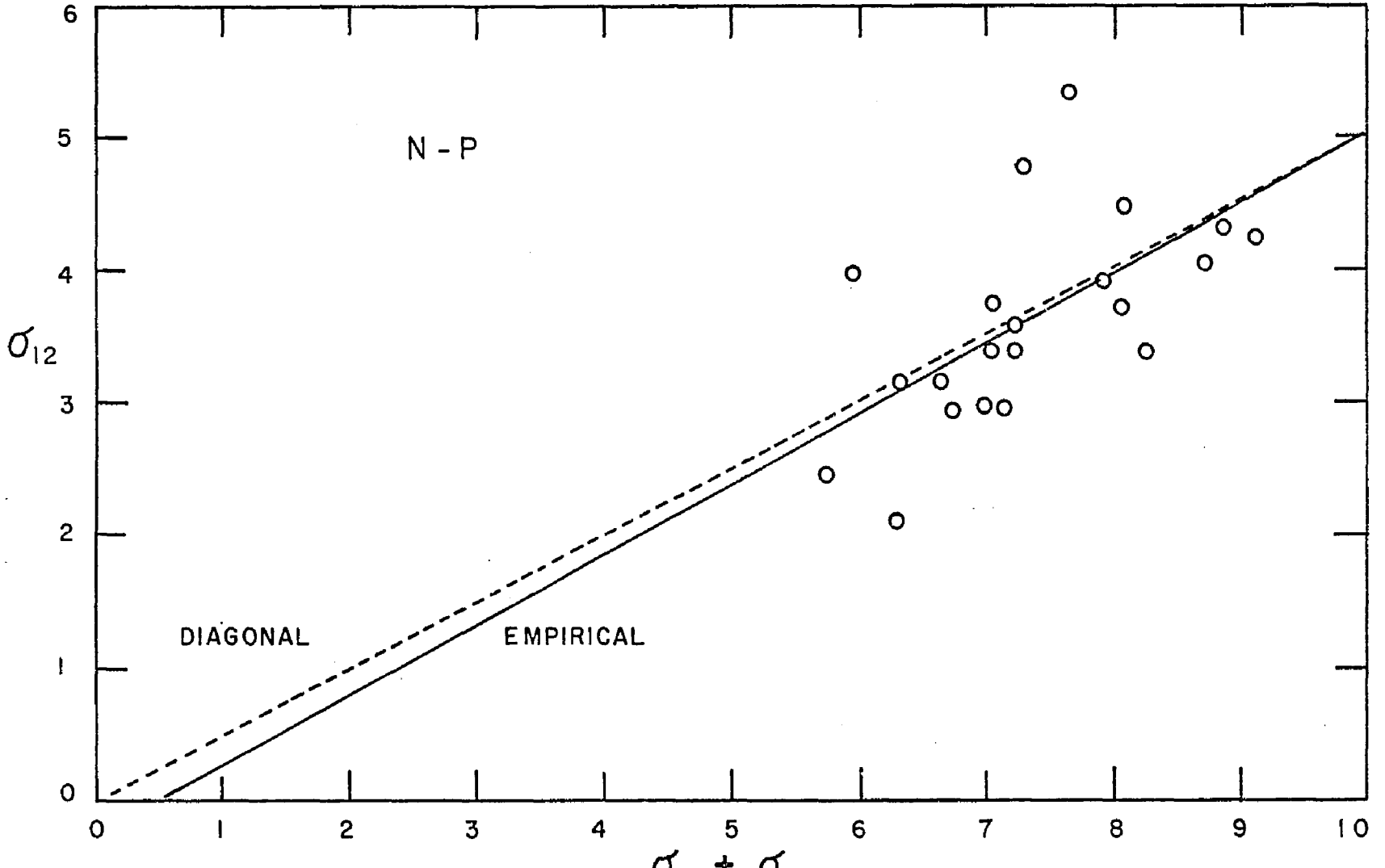


FIGURE-19· $\left[\sigma_{12}\right]_{DIFF.}$ VS $\left[\sigma_1 + \sigma_2\right]_{VISC.}$

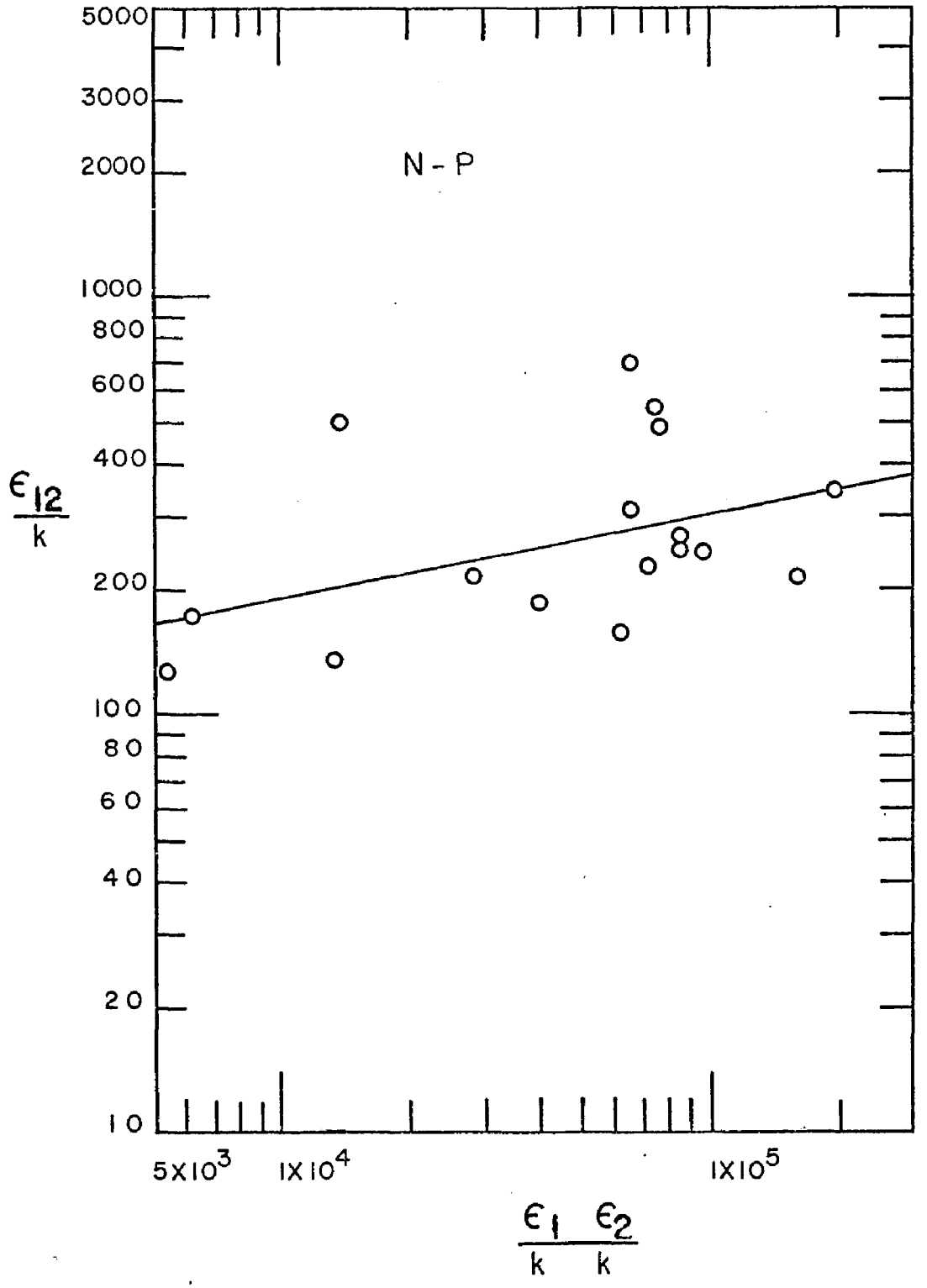


FIGURE - 20 · $\left[\frac{\epsilon_{12}}{k}\right]$ DIFF. VS $\left[\frac{\epsilon_1}{k}\ \frac{\epsilon_2}{k}\right]$ VISC.

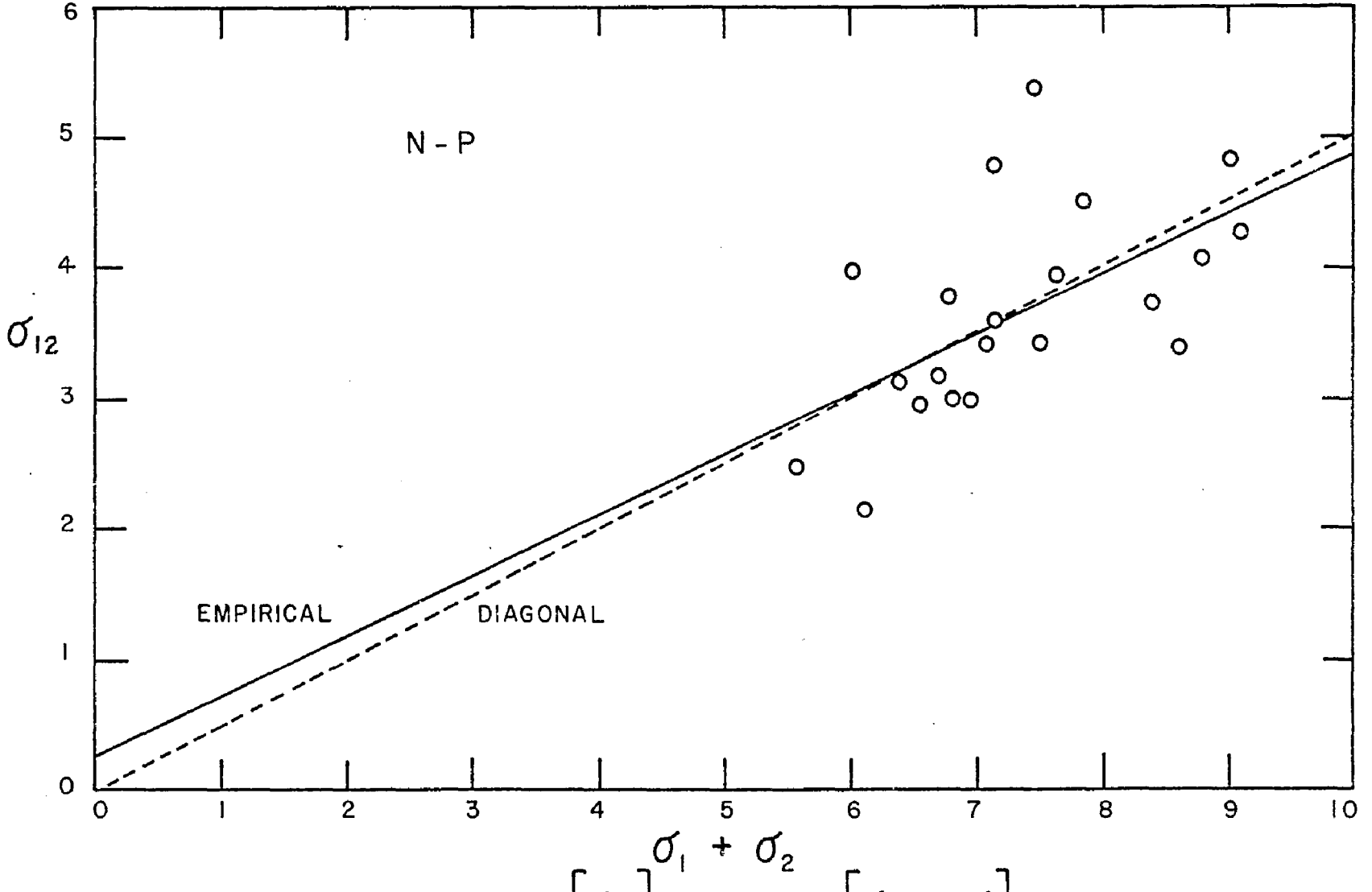


FIGURE- 21 · $\left[\sigma_{12}\right]_{\text{DIFF.}}$ VS $\left[\sigma_1 + \sigma_2\right]_{\text{VISC.}}$

(b) RESULTS ON THE MEASUREMENT OF DIFFUSION COEFFICIENTS:

The results of the present investigation, D_E and D_{12}, were expressed under conditions of standard pressure of one atmosphere and are presented here in the form of graphs and tables.

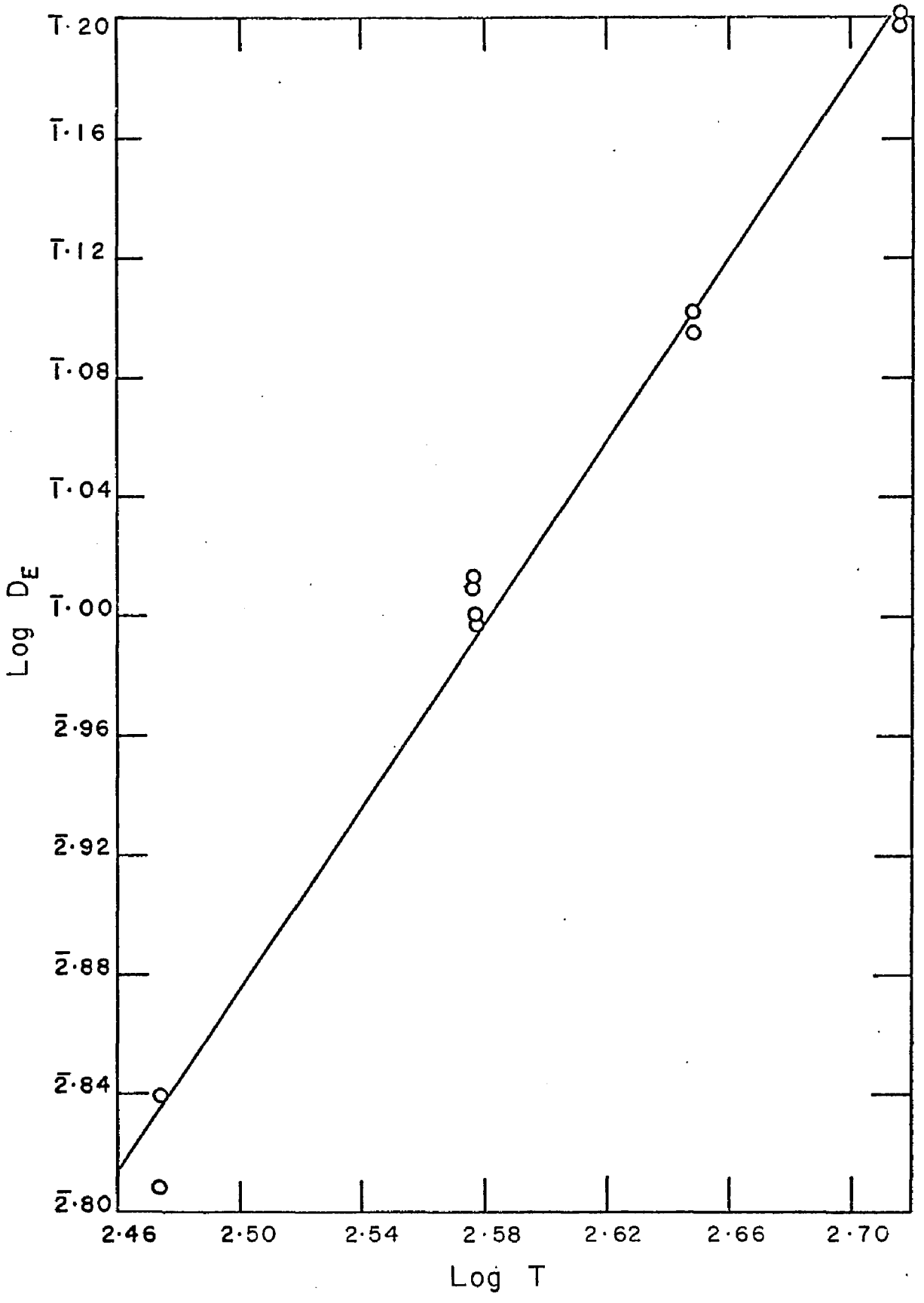
Figures 22, 23, & 24 show the effective diffusivities, D_E, for A - He ; He - N_2 ; and N_2 - CO_2 systems respectively plotted as Log D_E versus Log T. The best fitted curve for A - He system was a straight line with slope, β , equal to 1.5248, intercept, α , equal to - 4.9361 and standard deviation, σ , equal to $\pm$.0.012 ; that for He - N_2 system was a straight line with slope, β , equal to 1.5036, intecept, α , equal to - 4.9053 and the standard deviation σ , equal to $\pm$ 0.0048 ; and that for N_2 - CO_2 system was also a straight line with slope, β , equal to 1.5277, intercept, α , equal to - 5.5910 and the standard deviation σ , equal to $\pm$ 0.0042.

The ratios of the two diffusion rates of the above systems were compared with those calculated from Hoogschagen relationship and were found to be pretty close.

This is given in table - VII.

Figure 25 shows the diffusion cell calibration factor, γ , calculated from the true diffusivities, D_{12}, of the above systems measured by Walker and Westenburg [20] , and the effective diffusivities, D_E, of the same systems measured with the present diffusion cell, and plotted as γ , versus Log T. The best fitted curve in this case was a straight line with slope, β , equal to 6.1458, intercept, α , equal to - 4.0640 and standard deviation, σ , equal to $\pm$ 0.171.

Table - VIII gives a comparison of the true binary diffusivities of the above systems as a function of temperature as measured in this in-



A-He SYSTEM

FIGURE-22· Log D_E vs Log T

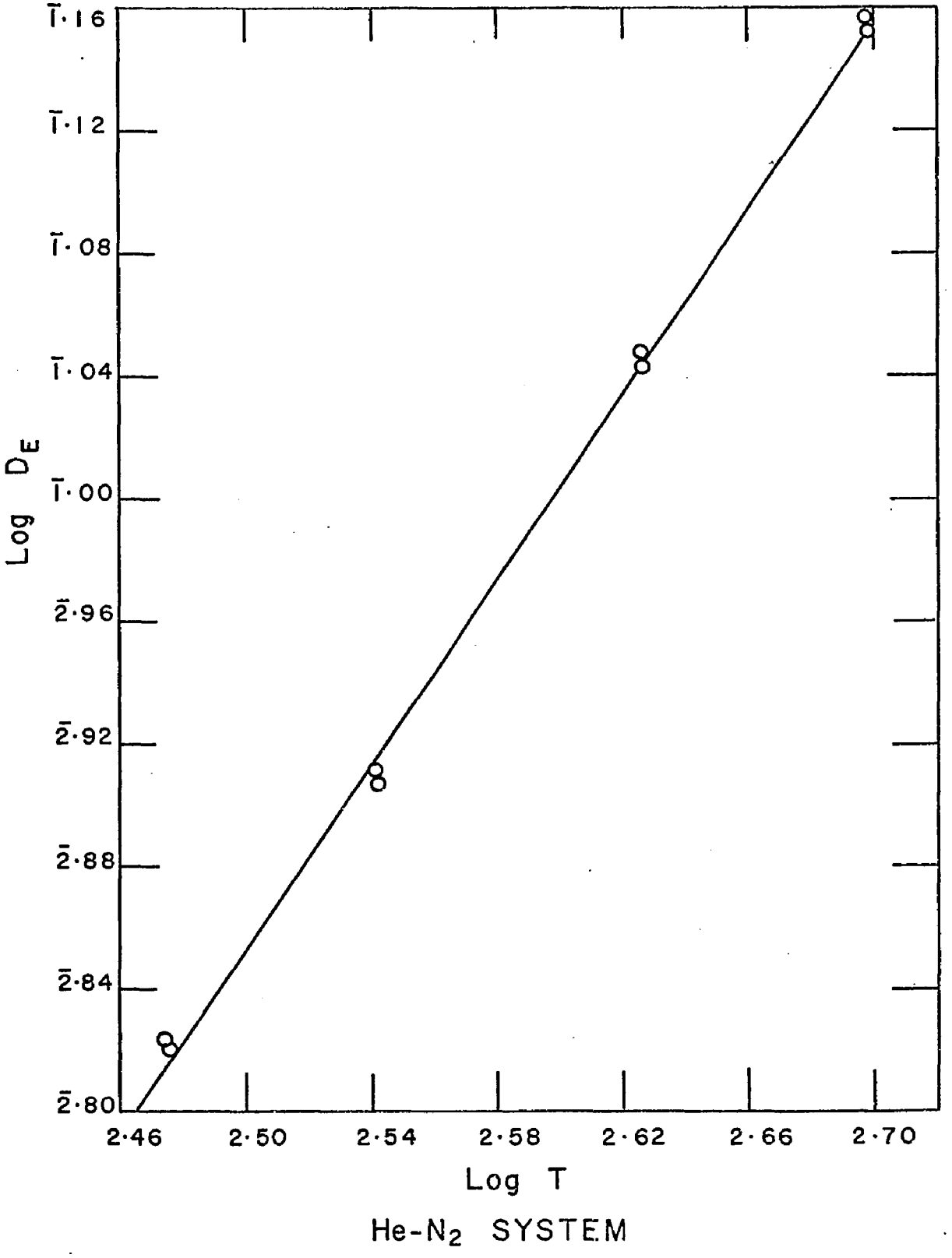
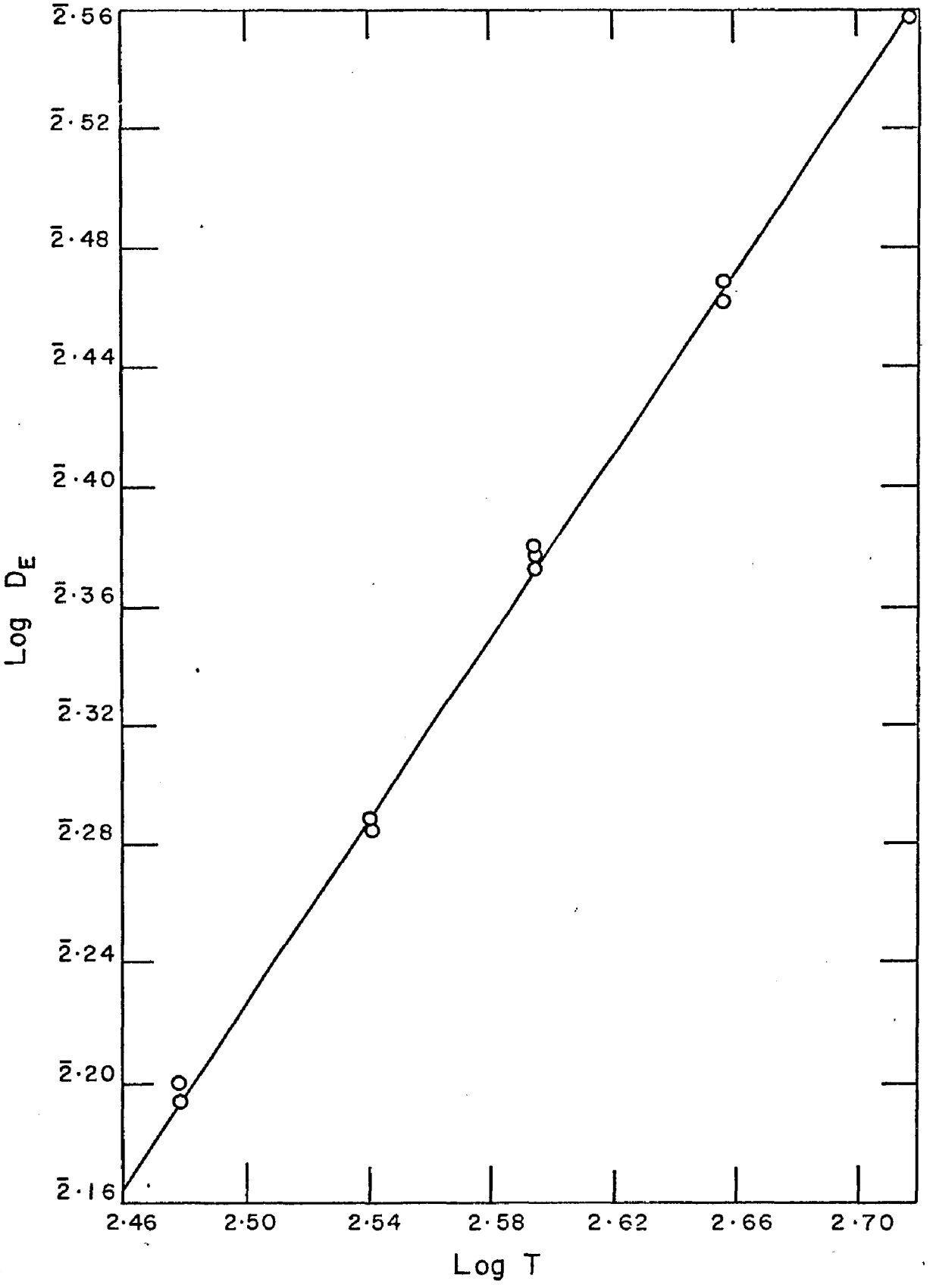


FIGURE-23· Log D_E VS Log T



N_2-CO_2 SYSTEM

FIGURE-24· Log D_E VS Log T

TABLE - VII

Comparison of the ratio of diffusion rates as observed with those predicted by Hoogschagen relationship.

Systems	Temperature ranges °K	$\sqrt{M_1/M_2}$ Hoogschagen's	$N_2/N_1 = V_2/V_1$ Observed
A - He	298 to 522	3.16	2.48 to 3.34
He - N_2	299 to 500	2.67	2.95 to 3.27
N_2 - CO_2	301 to 524.5	0.79	0.89 to 0.99

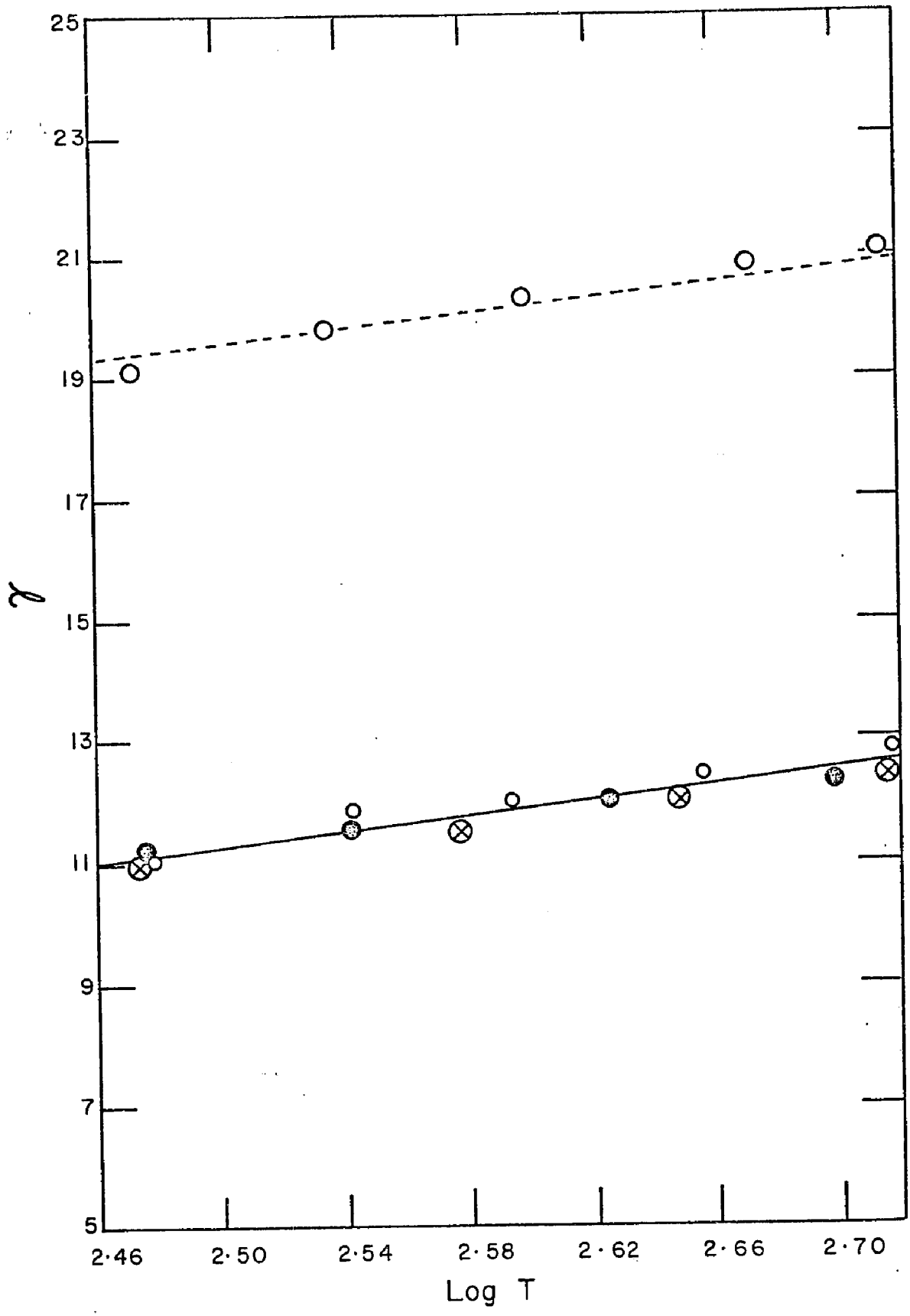


FIGURE - 25· γ VS Log T

TABLE - VIII

Comparison of the measured diffusivities with those obtained by Walker and Westenburg and those predicted by Hirschfelder's equation.

Systems	Temperature °K	D_{12}, $cm^2/sec.$		
		Present work	Walker and Westenburg	Hirschfelder
A - He	298.0	0.765	0.754	0.729
	378.0	1.162	1.142	1.083
	445.5	1.538	1.522	1.425
	522.0	2.040	2.007	1.854
He - N_2	299.0	0.732	0.739	0.704
	348.0	0.953	0.955	0.906
	423.0	1.336	1.328	1.254
	500.0	1.781	1.762	1.654
N_2 - CO_2	301.0	0.175	0.174	0.154
	348.0	0.221	0.226	0.200
	393.0	0.280	0.283	0.249
	453.5	0.360	0.365	0.321
	524.5	0.463	0.472	0.413

vestigation with those obtained by Walker and Westenburg as well as those predicted by Hirschfelder's equation using the Lennard-Jones (6-12) potential function.

Figures 26, 27, and 28 show the effective diffusivities, D_E, for N_2 - HCl, A - HBr, and N_2 - HBr systems respectively plotted as D_E vs log T. The best fitted lines in all the three cases were straight lines with respective slopes and intercepts as follows:

for N_2 - HCl system, slope, β, = 0.1115

intercept, α, = -0.2647

and standard deviation, σ, insignificantly small,

for A - HBr system, β = 0.0954

α = -0.2345

and standard deviation, σ is insignificant

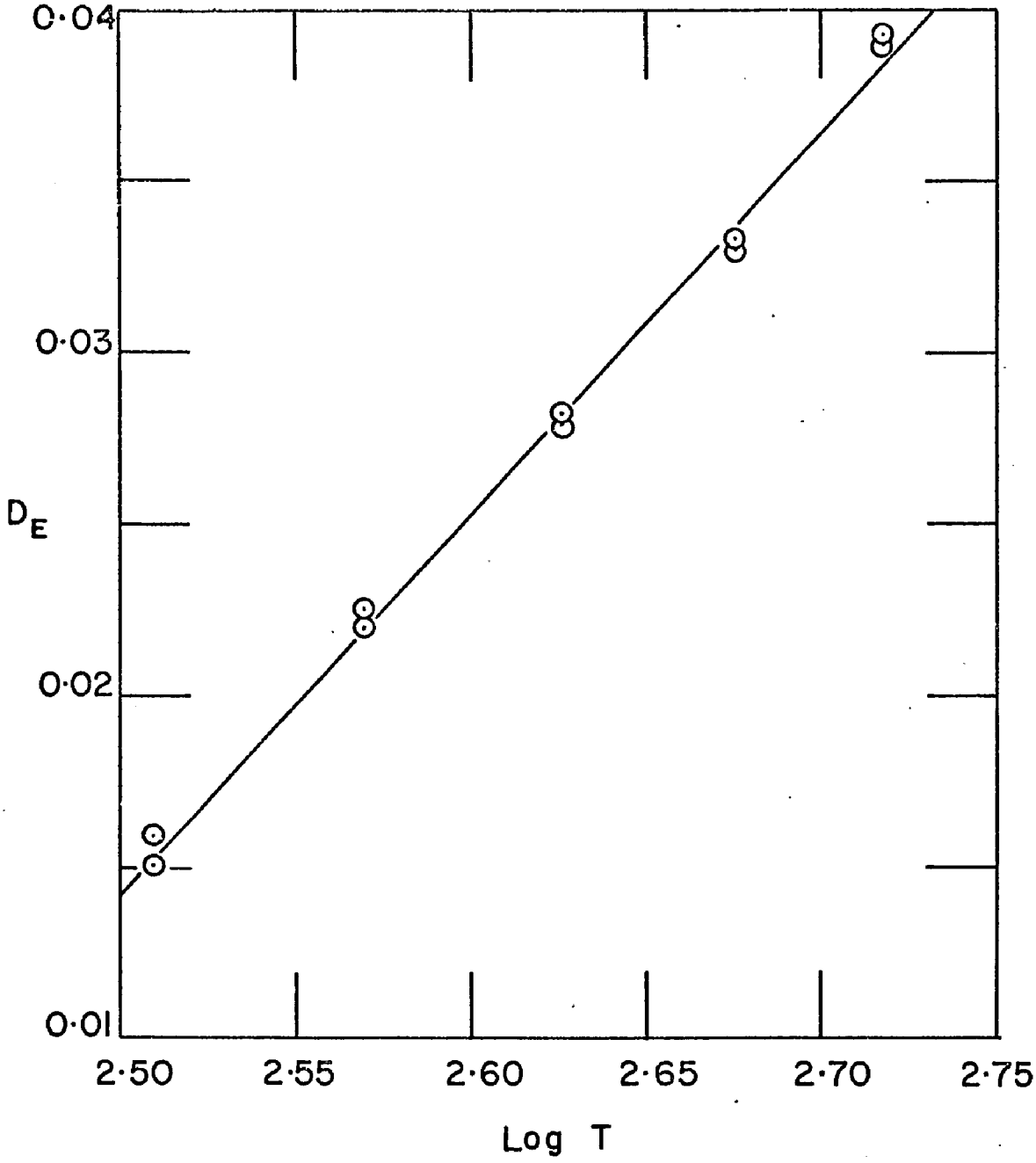
for N_2 - HBr system, β = 0.07820

α = -0.1839

and standard deviation, σ is insignificant.

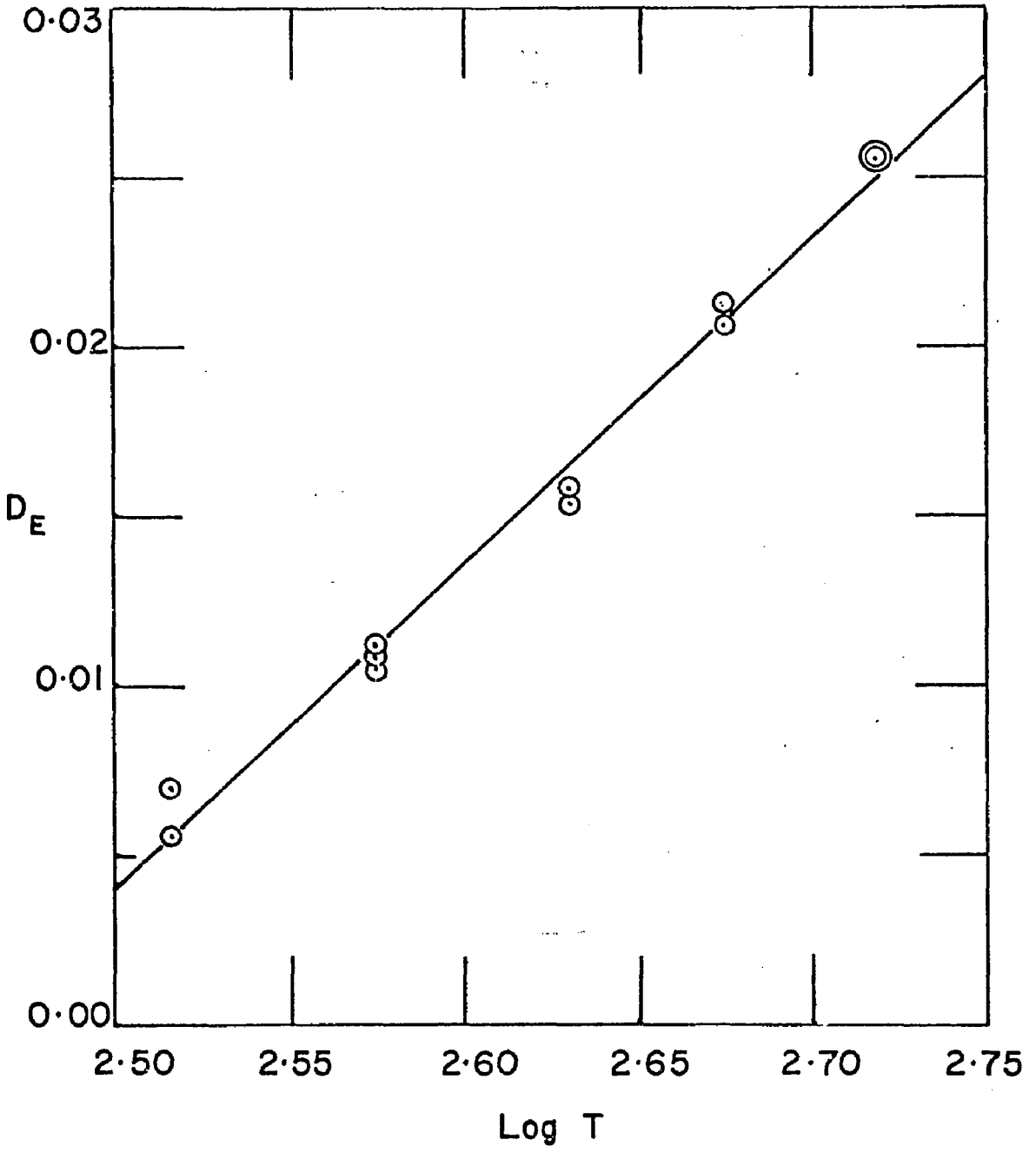
Table IX, Figures 29, 30, 31 compare the true diffusivities calculated from measured effective diffusivities of N_2 - HCl, A - HBr, and N_2 - HBr systems respectively with those predicted by Hirschfelder's equation (Eq. - 2), as well as Equation 27 and 28 employing empirical combining rules given by Equation 30 and 31.

Table X gives a comparison between the potential parameters given by Hirschfelder's combining rules (using Mason and Monchick's calculated parameters from viscosity data), those predicted by empirical equations 30 and 31, and the ones calculated from experimental diffusion data using the presently described direct method.



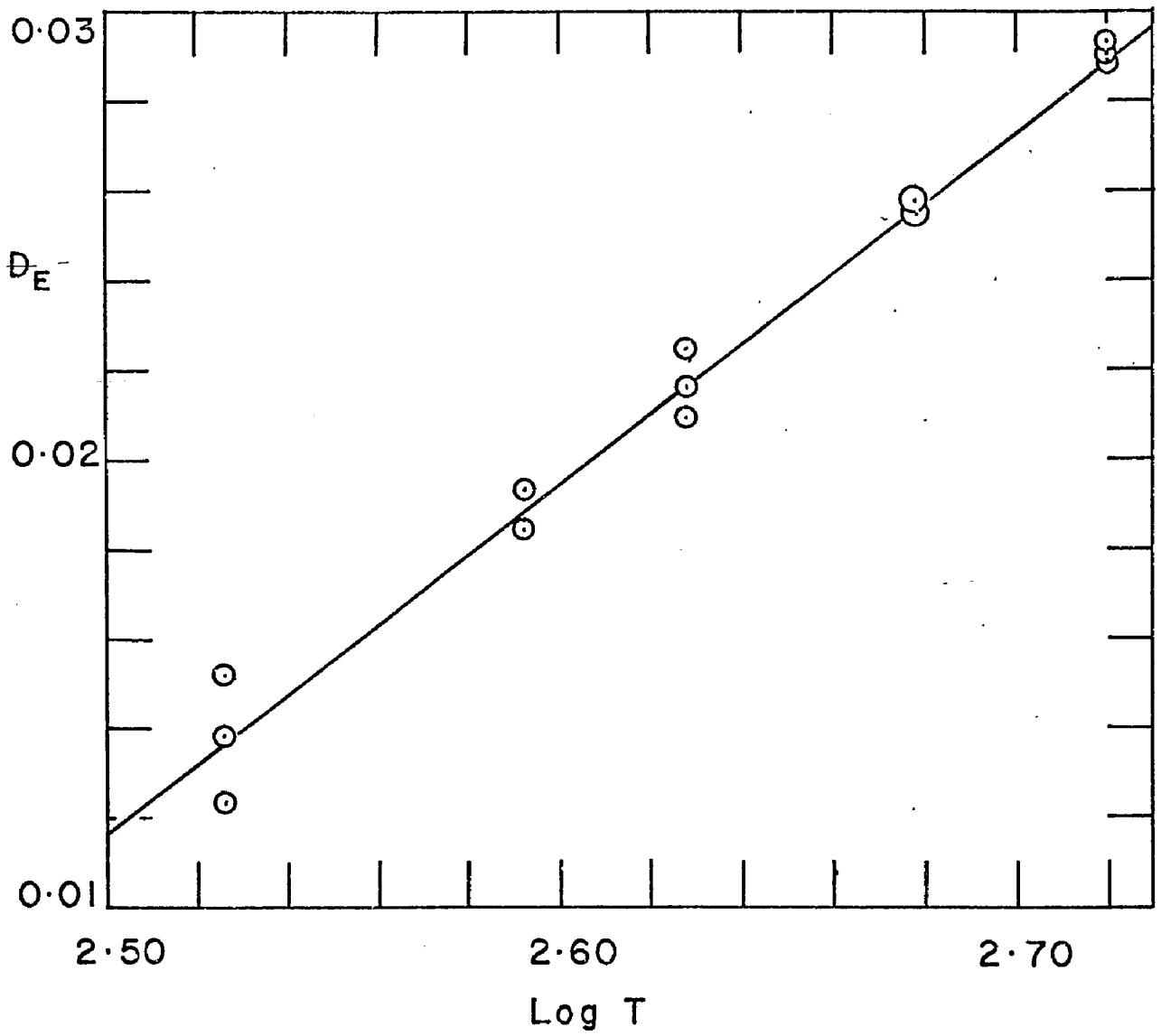
N_2-HCl SYSTEM

FIGURE-26· D_E vs Log T



A - HBr SYSTEM

FIGURE - 27· D_E vs Log T



N_2 - HBr SYSTEM

FIGURE-28· D_E vs Log T

TABLE - IX

Comparison of the measured diffusivities with those predicted by Hirschfelder's equation as well as by presently developed empirical equations.

Systems	Temperature °K	D_{12}, $cm^2/sec.$			
		Hirschfelder's Eq.	Empirical Eq. 27	Eq.28	Experimental
A - HBr	328.1	0.150	0.139	0.136	0.064
	375.1	0.197	0.185	0.181	0.131
	426.6	0.252	0.243	0.237	0.200
	472.6	0.302	0.302	0.295	0.257
	522.6	0.361	0.373	0.365	0.315
N_2 - HBr	336.1	0.180	0.170	0.162	0.157
	390.6	0.233	0.235	0.223	0.223
	424.6	0.275	0.280	0.266	0.261
	476.6	0.337	0.358	0.340	0.317
	525.1	0.400	0.440	0.418	0.365
N_2 - HCl	324.1	0.218	0.175	0.166	0.174
	373.1	0.278	0.235	0.224	0.260
	423.1	0.348	0.306	0.293	0.341
	474.1	0.427	0.390	0.372	0.418
	522.6	0.505	0.480	0.458	0.487

TABLE - X

Comparison of the potential parameters derived from diffusion data with those predicted by Hirschfelder's combining rule as well as by the presently developed empirical combining rules for the pure component parameters derived from viscosity data.

Systems	Parameter	Experimental	Mason and Monchick's (12 - 6)	Empirical equations No: 30 (12 - 6) (12 - 6) (12 - 6)	No: 31 (12 - 6) (12-6-3) (12 - 6)
A - HBr	ϵ_{np}/k,°K	654.38*	227.40	277.18	277.80
N_2-HBr		244.38	195.34	237.14	252.60
N_2-HCl		651.31*	137.61	222.73	254.60
A - HBr	σ_{np}, Å	3.110	3.414	3.102	3.198
N_2- HBr		3.510	3.545	3.279	3.352
N_2- HCl		2.625	3.520	3.487	3.431

* Systems marked asterisk did not follow (12-6) potential model.

VI DISCUSSION

Figure 6 shows that the more representative prediction equation for the binary diffusion coefficients of nonpolar - nonpolar systems than that of Hirschfelder, Bird etc. would be

$$D_{12}P = \frac{0.0026280\ T^{1.5}\left(\frac{M_1 + M_2}{2M_1M_2}\right)^{0.5}}{\left\{-0.0371 + 0.941\left[\sigma_{12}^2\ \Omega^{(1,1)^*}_{(T_{12}^*)}\right]_{L\text{-}J}\right.} \qquad \text{Eq. 23}$$

However it is a cumbersome equation to use. Somewhat more convenient than Eq. 23 is Eq. 24, obtained from the correlation of figure - 9.

$$D_{12}P = 0.000354\left(\frac{M_1 + M_2}{2M_1M_2}\right)^{0.5}\left(\frac{k}{\epsilon_{12}\ \sigma_{12}^2}\right)^{0.26}_{L\text{-}J}\left(T\right)^{1.76} \qquad \text{Eq. 24}$$

This equation involves the direct use of potential parameters and eliminates the tiresome evaluation of the collision integrals. The average deviation of experimental data from Eq. 24 is 5.3% which is somewhat better than that of Hirschfelder's prediction equation.

Eq. 24 is therefore recommended for prediction of diffusivities of nonpolar - nonpolar systems until a better purely theoretical equation is developed.

Correlations of nonpolar - polar systems in Figure - 7, employing (12-6) potential parameters for nonpolar components, (12-6-3) potential

parameters for polar components, and Hirschfelder's combining rules (given by Eq. 5) for the resultant potential parameters, give the representative prediction equation for diffusivities of nonpolar - polar systems as follows:

$$D_{12}P = \frac{0.0026280\ T^{1.5}\ \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{0.5}}{\left\{ - 0.8373 + 1.0867 \left[\sigma_{12}^2\ \Omega^{(1,1)*}_{(T_{12}^*)}\right]_{L\text{-}J}\right.} \qquad \text{Eq. 25}$$

Similar correlations in figure - 8, employing (12-6) potential parameters for the nonpolar, (12-6-3) potential parameters for the polar components and Hirschfelder's combining rules (given by Eq. 10) for the resultant potential parameters, gave a prediction equation that is given by Eq. 26.

$$D_{12}P = \frac{0.0026280\ T^{1.5}\ \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{0.5}}{\left\{ - 0.3372 + 1.0329 \left[\sigma_{np}^2\ \Omega^{(1,1)*}_{(T_{np}^*)}\right]_{STOCK.}\right.} \qquad \text{Eq. 26}$$

The standard and average deviations of experimental data from Eq. 26 were somewhat greater than those from Eq. 25. Nevertheless both of these equations are cumbersome to use and more convenient equations than these are obtained from correlations in figures - 10 & 11:

$$D_{12}P = 0.000632 \left(\frac{M_1 + M_2}{2M_1M_2}\right)^{0.5} \left(\frac{k}{\epsilon_{12}\sigma_{12}^2}\right)^{0.624}_{L\text{-}J} \left(T\right)^{2.124} \qquad \text{Eq. 27}$$

and

$$D_{12}P = 0.000639 \left(\frac{M_1 + M_2}{2M_1M_2} \right)^{0.5} \left(\frac{k}{\epsilon_{np}\sigma_{np}^2} \right)^{0.621}_{STOCK} \left(T \right)^{2.121} \qquad \text{Eq. 28}$$

Eq. 28 involves the calculation of ϵ_{np} and σ_{np} and is not of much advantage over Eq. 27, which gives somewhat better results than those of Hirschfelder's prediction equations using Lennard-Jones and Stockmayer's potential functions, and may be recommended for the prediction of diffusivities of nonpolar - polar systems for the time being.

Nevertheless the average deviation of experimental data from Eq. 27 is about 9% with a significant scattering. Whether this is due to faulty measurement of diffusion data or wrong estimation of the parameters of the potential functions involved in the correlations, is difficult to ascertain at this stage at least until dependable techniques are developed for the pertinent purposes.

The technique presently employed for the estimation of parameters of potential functions indicated that all gases (except neon), listed in Table III, followed (12-6) potential while all gases listed in Table IV might follow either (12-6) or 12-6-3) potential functions in their like-molecular interactions as evidenced from their viscosity data. Thus two sets of potential parameters were obtained for the second set of gases. Comparison of the parameters obtained by the present technique with those estimated by graphical method indicated large deviations in some cases while pretty closeness in others. Table V showed that even though the pure components followed (12-6) potential in their like-molecular interactions, in some cases they did not do so in nonpolar - nonpolar unlike-molecular interactions. Table VI showed that the diffusion data of most of the nonpolar-polar systems can be fitted to (12-6) type of potential

function. However the (12-6) potential parameters derived from diffusion data did not follow Hirschfelder's combining rules for those derived from viscosity data. Figures - 16, 18, and 20 showed correlations of energy parameters while figures - 17, 19, and 21 gave those of distance parameters derived from diffusion and viscosity data. The best fitted curves - least square straight lines - gave the following empirical combining rules:

(1) From figures 16 and 17, Nonpolar - nonpolar systems, following (12-6) potential functions in their like - as well as unlike-molecular interactions:

$$\left.\begin{aligned} \frac{\epsilon_{12}}{k} &= 0.01849 \left(\frac{\epsilon_1}{k} \cdot \frac{\epsilon_2}{k} \right)^{0.912} \\ \sigma_{12} &= -0.3711 + 0.6235 \ (\sigma_1 + \sigma_2) \end{aligned}\right\} \quad \text{Eq. 29}$$

(2) From figures - 18 and 19, Nonpolar - polar systems, following (12-6) potential functions in their like- as well as unlike-molecular interactions:

$$\left.\begin{aligned} \frac{\epsilon_{12}}{k} &= 7.353 \left(\frac{\epsilon_1}{k} \cdot \frac{\epsilon_2}{k} \right)^{0.328} \\ \sigma_{12} &= 0.24433 + 0.52727 \ (\sigma_1 + \sigma_2) \end{aligned}\right\} \quad \text{Eq. 30}$$

(3) From figures - 20 and 21, Nonpolar - polar systems, following (12-6) and (12-6-3) potential functions in their respective like-molecular interactions while (12-6) potential function in their unlike-molecular interactions:

$$\left.\begin{aligned} \frac{\epsilon_{np}}{k} &= 30.7 \left(\frac{\epsilon_1}{k} \cdot \frac{\epsilon_2}{k} \right)^{0.199} \\ \sigma_{np} &= 0.27879 + 0.4594 \ (\sigma_1 + \sigma_2) \end{aligned}\right\} \quad \text{Eq. 31}$$

In the derivation of the combining rules for the energy parameters the nonpolar - nonpolar systems not following (12-6) potentials in their like- and unlike-molecular interactions were not considered. Similarly the nonpolar - polar systems, not following (12-6) potentials in nonpolar like-molecular interactions and (12-6) or (12-6-3) potentials in their unlike-molecular interactions, were not considered for the energy parameters. However since the influence of energy parameters on pertinent distance parameters were found to be small, all systems were included in the correlations of distance parameters.

Experimental investigation indicated that the designed diffusion cell is suitable for the measurement of binary diffusion coefficients of any gaseous system that involves nearly spherical molecules. The standard error of estimate, about 2.0%, is considerably smaller than that associated with the Hirschelder's perdiction equation, and is of about the same order of magnitude as that associated with the so-called point source technique. The results of this measurement, therefore, are adequate for interpretation of the nature of the unlike molecular interactions which can be obtained from binary diffusion measurements.

The diffusion cell calibration factor, though varied with temperature, was found to be independent of the gas-pair constituting the diffusion system. This shows that this technique is a promising method for the measurement of binary diffusivities of gaseous systems having nearly spherical molecules. The temperature dependence of γ was found to be of the same general type for a plug with 10 micron nominal diameter as well as for one with 5 micron nominal diameter, tube diameter being 1.27 cm. in both cases. This is not desirable but then it is not a serious handicap as it can be evaluated over a wide range of temperature experi-

mentally.

The method, contrary to point source technique, is simple and the apparatus is easy to operate.

The effective diffusivities of A-He, He-N_2, and N_2-CO_2 gave in each case a straight line in a plot of log D_E vs log T whereas those of N_2-HCl, A-HBr, and N_2-HBr systems gave in each case a straight line in a plot of D_E vs log T. True diffusivities of N_2-HCl system were found to be somewhat lower than those predicted by Hirschfelder's equation and somewhat higher than those predicted by Eq. 28. They were pretty close to those given by Eq. 27. True diffusivities of both A-HBr and N_2-HBr systems were found to be lower than those predicted by Hirschfelder's equation as well as Eq. 27 and 28.

The data on A-HBr and N_2-HCl systems did not fit into the (12-6) potential model. Their temperature (or energy) parameters appeared to be much higher than the model can account for and greater than those predicted by either Hirschfelder's combining value or the empirical ones developed in Eq. 30 and 31. The distance parameters for N_2-HCl systems also seemed to be higher than the predicted ones, but that of A-HBr system was closer to that predicted by Eq. 30 and lower than those predicted by Eq. 31, and Hirschfelder's combined rule.

The data on N_2-HBr system did fit in the model but its energy parameter was found to be greater than those predicted by Hirschfelder's combining rule and Eq. 30 and small than that predicted by Eq. 31. The distance parameter was in agreement with that predicted by Hirschfelder's combining rule and greater than those predicted by either Eq. 30 or 31.

Recommendation for further works:

As it appears, the error in the estimation of the potential parameters is not the only reason of their scattering in the correlations presented here. Some property in the pertinent molecules which is hitherto not recognized is obviously contributing to the potential function involved. It does not seem to be one arising out of the chemical nature of the molecules as that would indicate a definite trend in the potential parameters for systems involving a family of compounds, like for example A - HCl, A - HBr, N_2 - HCl, and N_2 - HBr.

It may be guessed at this stage that this unidentified property may be the magnetic nature or property of the polar molecules that causes a magnetic force of attration between the nonpolar and polar molecules which is in addition to the electric dipole interaction. Depending on the intensity of magnetization in the molecules in question this magnetic force may be sufficiently stronger than the electric dipole interaction and thus cause the potential function to be different from Stockmayer's.

It is therefore recommended that the polar molecules be tested for magnetic property and that its effect on the potential function be correlated or established otherwise. This might for the case of polar - nonpolar systems lead to a potential function that contain a term of magnetic force (or energy) in addition to the dipole-induced dipole interaction, valence force and London dispersion force.

BIBLIOGRAPHIC REVIEW OF PERTINENT LITERATURE

Systems studies		Temperature Range of diffusion study in (°K)			Reference
Non polar - Non polar					
He	A	233.0	to	363.0	(17)
He	A	300		1100	(20)
Ne	A	90		437	(18)
Ne	A	273		318	(19)
Ne	Kr	274		318	(19)
Kr	A	90		437	(18)
Kr	A	273		318	(19)
Xe	A	194.7		378.0	(1)
He	N_2	300		1100	(20)
A	N_2	233		363	(17)
Ne	H_2	253		341	(12)
A	H_2	253		341	(12)
X_e	H_2	253		341	(12)
H_2	N_2	252		308	(17)
H_2	O_2	300		1100	(20)
H_2	CO_2	252		308	(17)
N_2	CO_2	252		308	(17)
N_2	CO_2	300		1100	(20)
O_2	CO_2	300		1100	(20)
O_2	Ch_4	300		1100	(20)

Systems studied		Temperature Range of diffusion study in (°K)			Reference
Non polar - Polar					
He	H_2O	307.1	to	352.4	(14)
O_2	CO	300		1100	(20)
H_2	H_2O	307.1		352.4	(14)
N_2	H_2O	307.1		352.4	(14)
Air	H_2O	298.9		332.0	(3)
O_2	H_2O	307.9		352.2	(14)
H_2	CH_2OH	273		322.6	(7)
Air	CH_3OH	273		322.6	(7)
H_2	C_2H_5OH	273		339.9	(7)
Air	C_2H_5OH	298.9		332.0	(3)
Air	Isopropyl Alcohol	298.9		332.0	(3)
Air	Sec-Butyl Alcohol	298.9		332.0	(3)
Air	n-Butyl Alcohol	298.9		332.0	(3)
Air	Sec-amyl Alcohol	298.9		332.0	(3)
Air	Ethyl-acetate	298.9		332.0	(3)
Air	Toluene	298.9		332.0	(3)
Air	Aniline	298.9		332.0	(3)
Air	Chlorobenzene			332.0	(3)
CO_2	H_2O	307		352.2	(14)
CH_4	H_2O	307.5		352.1	(14)
C_2H_4	H_2O	307.6		352.4	(14)
CO_2	CH_3OH	273		322	(7)
CO_2	C_2H_5OH	273		339.9	(7)

Systems studies		Temperature Range of diffusion study in (°K)		Reference
Non polar - Polar				
NH_3	Ar	254.7	333	(19)
NH_3	KR	254.7	333	(19)
HCl	Ar	297	523	(10)
SO_2	Ar	294	522	(10)

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VITA

Aziz Ahmed Mian, son of Moulvi Latif Ahmed Mian, was born in the village of Sadipur of the district of Malda, West Bengal, presently under the territory of the Republic of India, on the 1st day of August, 1925. He was educated in the Mohanpur Primary School, GabindaGange Primary Maktab, Bangitolla M.E.School, and the Malda Zilla School, Malda. After being matriculated from the Malda Zilla School in March, 1941, he entered into the Rajshahi Government College, Rajshahi, presently under the territory of the Islamic Republic of Pakistan, and received the degree of Bachelor of Science with Distinction in March, 1946, conferred by the University of Calcutta. The combination of his courses was Physics, Chemistry, and Mathematics besides English and Vernacular, Bengali. He then entered into the Aligarh Muslim University, Aligarh, India, in August, 1946, and received the degree of Master of Science in Chemistry in April, 1948.

He served as a lecturer of Chemistry in Satkhira College, Khulna, East Pakistan, after receiving his degree of Master of Science until the end of August, 1951. In September, 1951, he was appointed a lecturer of Chemistry by the Government of East Pakistan and posted in the Eastern Pakistan College of Veterinary Science and Animal Husbandry, Tejgaon, Dacca, East Pakistan. He taught General Chemistry in the same college for five years and then resigned on January 31, 1957, with the intention of coming over to the United States of America for higher studies.

In March, 1957, he entered into the Alabama Polytechnic Institute, Auburn, Alabama, as a junior and received the degree of Bachelor of Science in Chemical Engineering in August, 1958. The same year, in

September he entered the Graduate School of the Alabama Polytechnic Institute as a teaching assistant in Chemistry while working for a higher degree in Chemical Engineering. He was duly initiated as a member of the national honorary chemical society, Phi Lambda Upsilon, by the Alpha Iota Chapter of the Alabama Polytechnic Institute, Auburn, on the 20th day of November, 1958, for his high scholastic record and promise in the field of chemistry and chemical engineering. On the 2nd day of July, 1959, he was elected a member of the national honor society, Phi Kappa Phi, and in August same year he received the degree of Master of Science in Chemical Engineering. In September, 1959, he moved to Canada to enter the University of British Columbia, Vancouver, Canada, as a research assistant.

On the 12th May, 1961, he married Suraiya Sultana, daughter of Khan Bahadur Chowdhuri Afsar Ali, of Wari, Dacca, East Pakistan, who migrated from Alinager, Murshidabad, presently under the territory of the republic of India. They were blessed with a sweet and beautiful daughter, Shayela Nazneen Ahmed Mian, o/f Thina, on the 9th July, 1962. In October same year he was awarded the degree of Master of Applied Science persuing through Chemical Engineering.

He then entered the Louisiana State University, Baton Rouge, Louisiana, as graduate assistant to work for the Ph.D. degree. On March 26, 1964, they were blessed with a second sweet and beautiful daughter, Ayesa Nazneen Ahmed Mian, o/f Nina. On the 28th May, 1964, he was honored with a membership of the national honor society for the American Scientists, The Society of Sigma XI. In August, 1965, he accepted a full-time employment with the Louisiana State Department of Revenue to work as supervisor of the Motor Fuel Laboratory. Since then he conducted his research in the

department of chemical engineering at night i.e. after rendering his services at the Motor Fuel Laboratory. He finished his experimental research in August, 1966, and moved to Wilmington, Delaware to work for E.I.Du Pont de Nemours & Company as a research engineer. While working at Wilmington he wrote his dissertation and submitted to the Department of Chemical Engineering of Louisiana State University for evaluation. At the Wilmington experimental station he was elected a member of the Scientific Research Society of America.

EXAMINATION AND THESIS REPORT

Candidate: Aziz Ahmed Mian

Major Field: Chemical Engineering

Title of Thesis: Measurement and Prediction of Binary Gaseous Diffusion Coefficients

Approved:

Jesse Coates
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Albert Hweba

Frank R. Groves Jr.

Paul W. Murrill

Ralph W. Pike

Date of Examination:

Wednesday, July 5, 1967